535204

Department of Applied Geology

Fluoride Contaminated Drinking Water in Gokwe District (NW Zimbabwe): Spatial Distribution, Lithostratigraphic controls and Implications for Human Health

Antony Mamuse

This thesis is presented for the Degree of
Master of Science (Applied Geology)
of Curtin University of Technology

March 2003

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

Signature: ....

Date: ....

Frontispiece: Young victims of dental fluorosis, Gokwe District, NW Zimbabwe.

ACKNOWLEDGEMENTS

This research and precursor studies were undertaken during the tenure of an AusAID scholarship. I would like to acknowledge the perennial support I received from Deb, Julie and Anita of the AusAID Liaison Office at Curtin University of Technology.

Fieldwork was financially and materially supported by EIGG (Environmental Inorganic Geochemistry Group, Curtin University of Technology) and the ZGS (Zimbabwe Geological Survey). Foremost, I would like to thank my supervisor Ron Watkins for guidance, sound advice and thoughtful comments throughout this project. I am also grateful to my colleagues at the ZGS for their assistance and support. Forbes Mugumbate is credited for recommending and supporting this project. Ali Ait-Kaci Ahmed and Artwell Mukandi provided eye-opening comments during the reconnaissance phase of this project. Ali unfailingly continued to ply me with valuable information through correspondence. Bornwell Mupaya imbued me with a wealth of research and write-up tips. Warren Makamure provided unwavering logistical and technical assistance in the field. Wilmose Mafuse deserves special mention for accompanying me across the border into Zambia to attend to certain logistics of the project. Peter is thanked for sample preparations. Richard Owen of the University of Zimbabwe provided advice and supplied a water level dip meter. My colleagues at EIGG, namely Ryan, Troy, Dave, Eddie, Bob and John are thanked for logistical, technical and social support throughout my two years at Curtin and during the course of the project.

I was privileged to spend three months at the GSWA (Geological Survey of Western Australia) learning aspects of GIS that helped shape this project. I would like to thank Tim Griffin (Director) and all staff at GSWA, particularly Andrew Goss (organizer/ process leader) and the staff at the Geoscience Data Management Section for their support and patience. Lindsay Collins (Head of the Department of Applied Geology, Curtin University) is thanked for arranging the work experience program through which I was involved with GSWA.

Finally, I am indebted to my wife Dealia and son Precise for their forbearance to my prolonged mental absences from family life caused by this enterprise.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

FIGURES

TABLES

ABBREVIATIONS USED IN THIS THESIS

CDTA	Cyclohexylene Dinitrilo Tetraacetic Acid
CSIR	Centre for Scientific and Industrial Research (S. Africa)
DEP	Department of Environmental Protection (USA)
EIGG	Environmental Inorganic Geochemistry Group
ESRI™	Environmental Systems Research Institute
FISE	Fluoride Ion Selective Electrode
GIS	Geographical Information System
GSWA	Geological Survey of Western Australia
HPIC	High Performance Ion Chromatography
IDW	Inverse Distance Weighted
MSL	Mean Sea Level
NRC	National Research Council (U.S.A)
ppb	parts per billion
ppm	parts per million
TISAB	Total Ionic Strength Adjustment Buffer
TDS	Total dissolved solids
UNICEF	United Nations International Children and Education Fund
UTM	Universal Transverse Mercator
WHO	World Health Organisation
ZGS	Zimbabwe Geological Survey
ZINWA	Zimbabwe National Water Authority

ABSTRACT

The supply of drinking water in Gokwe District (NW Zimbabwe) is almost entirely based on groundwater drawn from boreholes and open dug wells. In certain areas of the district, the occurrence of dental fluorosis has been linked to excessive fluoride in the water supplies. A high prevalence of dental fluorosis (about 62%) was previously recorded among school children in the district. The aim of this study was to determine relationships between the spatial distribution of fluoride content in drinking water supplies in Gokwe, and lateral and vertical geological variation.

A total of 224 water samples were collected from 196 water sources in the study area (a further 18 water sources just outside the study area were also sampled). All the samples were analysed for fluoride in the field using the fluoride ion selective electrode method (FISE). One hundred and fifty nine duplicate samples were analysed for fluoride and common anions and cations using High Performance Ion Chromatography (HPIC) in the laboratory. Two main groups of computer programmes were employed: (1) Geographic Information System (ArcView® GIS) was used to store, analyse and display multiple layers of surface geologic and geographic information, and (2) a three-dimensional visualisation programme (Rockworks) was used to interpret and illustrate site stratigraphy based on borehole information.

Results indicated that the fluoride content of drinking water in the study area ranges from 0 to 9.65 mg/L. Forty-seven water sources (24%) yielded water containing fluoride in excess of the World Health Organisation's (WHO) health limit of 1.5 mg/L F. Of the 47 high fluoride water sources, 43 were boreholes (pumped or artesian). The shallower water sources (dug wells, streams and dams) largely yielded low-fluoride water. The groundwater fluoride contamination is stratigraphically controlled and originates from carbonaceous material (carbonaceous shales, carbonaceous mudstones and coaly material) within the Lower Madumabisa and Middle Wankie Members of the Lower Karoo Group. It has been shown that in general the greater the proportion of carbonaceous material intersected by a borehole, the greater the fluoride concentration of the water. Probable mineral sources of fluoride within the carbonaceous material include fluorapatite, kaolinite and trona. Chemical parameters that appear to influence the concentration of dissolved F in the water supplies include total dissolved solids (TDS), NaCl and pH. In relatively low fluoride waters, F concentrations generally increase with TDS and NaCl concentrations, whereas the highest F concentrations are found in moderately alkaline (pH 7.8-9) waters.

Based on ranges of fluoride concentration in drinking water, fluorosis-risk zones were identified and have been illustrated on a fluorosis-risk map. The zones are: No Risk Zone (0-1.5 mg/L F), Moderate Risk Zone (1.5-3.0 mg/L F), High Risk Zone (3.0-6.0 mg/L F) and the Very High Risk Zone (6.0-10.0 mg/L F). The map suggests that groundwater available to people occupying 3650 km^2 (60.8%) of the study area potentially contains excessive fluoride (F>1.5 mg/L), presaging the occurrence of dental fluorosis, skeletal fluorosis and crippling skeletal fluorosis in the area.

Different strategies may be employed to ameliorate the fluoride problem in Gokwe.

These include sinking new boreholes to optimal depths and in appropriate locations, promoting the use of surface water and shallow groundwater, resettlement and defluoridation. However in order to fully understand the problem and to prescribe these or other solutions more comprehensively, multi-disciplinary studies may be required. Such studies may consider isotopic dating of water to investigate any relationships between fluoride concentration and residence time of water, geochemical analyses of rocks and soils, detailed fluorosis epidemiology studies and test-scale defluoridation investigations.

1

INTRODUCTION

1.1 Background To Study

This research was undertaken to explore and understand the possible relationship between groundwater quality and geological materials and processes with respect to the suspected occurrence of endemic fluorosis in Gokwe District, NW Zimbabwe. Significant human settlement in the district commenced only in the mid sixties after eradication of tsetse fly. The new settlements were initially established close to rivers but with the subsequent drilling of water supply boreholes, settlements promulgated. Additional boreholes, initially drilled for coal exploration purposes, most with artesian flow, also became available for water supply. However, after several years of utilising borehole water, children in certain areas of Gokwe developed discoloured and disfigured teeth.

During a government-commissioned rural water project in the mid 1980s it was discovered that water from some boreholes in Gokwe and other parts of Zimbabwe contained excessive fluoride. Tobayiwa et al. (1991) conducted a water sampling and epidemiological survey in Gokwe and Chimanimani District (eastern Zimbabwe). The results of their study indicated that fluoride poisoning was prevalent in Gokwe, but the study did not address the possible association of fluoride distribution with environmental factors, such as geological processes and materials. This omission is understandable given that the research team did not include a geoscientist.

For some time, the Zimbabwe Geological Survey (ZGS) has considered adding to its core activities projects, environmental or otherwise, that are directly relevant to societal needs and problems. This project was proposed following separate observations by two geologists of the ZGS of an unusually high number of people with discoloured and disfigured teeth in Gokwe.

1.2 Fluorine and Health: Selected Case Histories

Fluorine is generally considered to be beneficial for human health and development, but excessive intake of the element may generate adverse health effects. In many parts of the world, naturally excessive fluoride in drinking water has been linked to widespread fluorosis, a disease characterised by discoloured and mottled teeth (dental fluorosis) or by severe permanent bone and joint damage (skeletal fluorosis). There are several other toxic effects linked to fluoride, but fluorosis is one of the most widespread and best documented.

One of the earliest known reports of fluorosis emanated from Durango, Mexico when in 1888, members of a family were famed for their "black teeth" (WHO 2000). In 1891, dental mottling was reported among inhabitants of Naples and in 1901, Frederick McKay a dentist in Colorado, USA, described 'Colorado brown stain' in his patients (Eager, cited in WHO 2000; Martin 1991; NRC 1993). In 1931, with the help of a chemist, McKay obtained a chemical analysis of water from some drinking water sources in Colorado. The analytical results led him to suggest a direct relationship between the fluoride concentration in drinking water and the disfigurement of teeth. Contemporaneously, MC

Smith, EM Lantz and HV Smith in Arizona succeeded in inducing dental mottling in rats by feeding them fluoride and in the same year, H Velu reported the link between fluoride and mottling of teeth based on studies in Morocco and Tunisia (Martin 1991). In response to the mounting claims, the United States Public Health Service (USPHS) assigned H. Trendley Dean to investigate the condition and Dean (1934; 1942) recommended that the optimum concentration of fluoride in drinking water should be set at 1.0mg/L. Subsequently dental fluorosis was reported in many other parts of the world. The World Health Organisation (WHO) currently sets the maximum contaminant level (MCL) of fluoride in drinking water at 1.5 mg/L (WHO 1984; 1996; 2000).

Recent literature suggests fluorosis is a global problem affecting more than 70 million people in 25 countries (Andezhath & Gosh 1999; WHO 2000; UNICEF 2002). Owing to the widespread occurrence of fluorosis, many studies have been conducted on virtually all continents to determine the prevalence and severity of fluorosis in relation to the concentration of fluoride occurring naturally in drinking water. An important distinction should however be made between the fluoride problem in developed countries and in developing countries. In developed countries, drinking water is no longer considered to be the only significant source of fluoride exposure because of major contributions from ubiquitous dental products, fluoride supplements, varied foodstuffs and infant formulas (NRC 1993; WHO 1996; 2000). However in developing countries, particularly in rural communities, these products are generally rare and portable water is the major source of fluoride. Thus the concentration of fluoride in drinking water in these communities is a reasonable surrogate for fluoride exposure (WHO 2000).

In Sri Lanka several researchers have found that the prevalence of fluorosis in the population of the Dry Zone where fluoride concentration in groundwater is as high as 10mg/L, ranges from 51 to 78 % (Dissanayake 1996). In contrast, the fluorosis prevalence in most of the Wet Zone, with fluoride concentrations below 1.5 mg/L was found to be 5.4%. The lower fluoride concentrations were attributed to the dilution of fluoride by water abundantly available in the environment.

Choubisa (1998) conducted fluorosis research among villagers in Udaippur District (Rajasthan, India) and found that they and their livestock were exposed to 0.3-7.0mg/L fluoride in drinking water. He reported that at the mean concentration of 5.8 mg/L F, 100% of adults and 88.7% of children (<18 years) were affected by dental fluorosis and 42% of the total population was affected by skeletal fluorosis. The results also suggested that the prevalence of skeletal fluorosis was higher among males than females and that fluorosis prevalence and severity increased with increasing fluoride concentration and with age. Among the animals, buffaloes were more affected in terms of prevalence and severity of both dental and skeletal fluorosis than cattle, and calves of both were more affected than mature animals. Sheep and goats were virtually fluorosis-free.

In Togtoh County (Inner Mongolia, China) Wang et al. (1999) found that 62% of the water supply wells yielded water with fluoride at concentrations higher than 1.5ppm, with the highest value being 8.0ppm. They reported a 53% prevalence of fluorosis and suggested a positive correlation between morbidity and fluoride concentration.

Alarcón-Herrera et al. (2001) reported fluoride levels of up to 5.4 mg/L in a study in Guadiana Valley (Durango City, north-western Mexico). In the environs just outside the city, they reported concentrations of up to 16mg/L F. They were able to draw a linear correlation between the severity of fluorosis and the fluoride concentration in the water.

Apambire et al. (1997) conducted a study in an area in the upper regions of Ghana where the prevalence of fluorosis was known to be up to 62% in school children. They found that fluoride levels in water from groundwater supply wells ranged from 0.11-4.60 mg/L. The higher values were thought to be associated with a coarse-grained hornblende granite and syenite suite. 49% of the wells delivered water with fluoride concentrations below the optimum level of 0.5 mg/L, putting populations at the risk of dental caries; 28% delivered water with the optimum fluoride range of 0.5-1.5 mg/L whilst water from the remaining 23% had concentrations above 1.5 mg/L F, exposing people to the risk of fluorosis.

McCaffrey (1998) found that the distribution of fluoride in groundwater in the Western Bushveld area of South Africa varied with rock type. He reported the following mean fluoride concentrations: 0.4mg/L (Rustenburg Layered Suite), 3.9 mg/L (Lebowa Granite Suite), 2.0mg/L (Nebo Granite Suite), 15.0mg/L (Pilanesberg Complex Nepheline Syenite), and 2.3mg/L (Ecca shales). He drew correlations between the fluoride levels in the groundwater and the fluoride content of the aquifer units and suggested that most of the fluoride originated from dissolution of F-bearing minerals, principally fluorite.

1.3 Fluorosis in Zimbabwe: Previous Work

In Zimbabwe, fluorosis was first recognised during the 1980-1990 United Nations Water and Sanitation Decade when the government contracted a consulting company, INTERCONSULT^{AS} to prepare a 'National Master Plan for Rural Water Supply and Sanitation'. Based on a very low-density regional scale water sampling exercise, INTERCONSULT^{AS} (1985) reported that drinking water from some sources in at least four districts in Zimbabwe, including Gokwe District, contained excessive fluoride, which could cause fluorosis. INTERCONSULT^{AS} (1985) suggested that in Gokwe District, excessive fluoride was mainly confined to artesian boreholes tapping water from the Wankie Formation aquifer. In a short report on table salt prospectivity in Gokwe, Magalela (1997) suggested that observed cases of dental mottling in some localities in Gokwe might be a result of excessive fluoride in the drinking water in the area. He speculated that the fluoride might be associated with basaltic rocks of the Karoo in the area.

Tobayiwa et al. (1991) conducted the first local-scale fluorosis study in Zimbabwe. They analysed water samples collected from water sources within the catchments of selected schools in Gokwe (western Zimbabwe) and Chimanimani (eastern Zimbabwe) districts, and carried out dental surveys among school children from the selected schools. The authors found that the prevalence of dental fluorosis among the examined school children was 61.9% in Gokwe and 66.2% in Chimanimani, and they explained the high prevalence in terms of excess fluoride (up to 5ppm in Chimanimani and ranging between 7 and 10ppm in Gokwe). Tobayiwa et al. (1991) suggested that in Chimanimani the high fluoride water emanated from hot springs while in Gokwe it emanated from artesian wells. The study however had two major limitations. Firstly, the data collected did not have a precise spatial reference system and it used school catchments, which had not been delineated and which are very dynamic, as the only objects of reference. Secondly, the research did not take into account environmental variables such as the type and composition of aquifer units and overall water chemistry, which are potentially important factors in fluoride distribution and bioavailability.

1.4 Purpose and Significance of This Study

The purpose of this thesis is to determine any spatial variations of drinking water quality parameters (with a particular interest in fluoride content) in Gokwe, with lateral and vertical geological variation. The findings of this research may be useful in several theoretical and practical ways:

1. The results of this study could be of importance in understanding the correlations of geology and hydrogeology with fluoride occurrence and distribution.

2. Pursuant to (1) above, this study will demonstrate the application of a GIS to process spatial geological data to determine the relation between groundwater quality parameters and geologic units. It will also be shown that the functionality of the GIS can be enhanced via coupling with modelling software to determine variations in the third dimension.

3. The research may contribute to the body of knowledge regarding the influence of other ions in the environment on fluoride occurrence and bioavailability.

4. The fluorosis-risk map resulting from this study may be used:
    i. In the determination of the appropriate location and depth of future drinking water boreholes in the area of study.

    ii. By health officials as a sound basis for planning epidemiological studies and health education programmes in the area.

    iii. By clinicians in screening patients on the basis of the location of a patient's residence on the geochemical health-risk map. This is useful because the signs of fluorosis commonly overlap with symptoms of other diseases.

5. Results of this study could help generate awareness among professionals leading to the adoption of multi-disciplinary approaches in providing safe drinking water, such as devising fluoride removal technologies and strategies.

6. This study may point to the need for similar research in other parts of the Zimbabwe and other countries in the region.

2

THE STUDY AREA

2.1 Location of the Study Area

The study area (Fig. 2.1), which lies in the administrative district of Gokwe in western Zimbabwe, covers an area of about 6 000 km^2. The approximate UTM coordinates bounding the area are:

0660000 and 0740000 East

8010000 and 8070000 North

For reference purposes, the area will be subdivided into:

1. Central part: the area coinciding with the geological map of Ait-Kaci Ahmed (*in prep.)* bounded by the following coordinates:

   659254 and 712354 East

   8008845 and 8064185 North

2. Eastern part: the area to the east of the central part which is covered by a part of the geological map of Leyshon (1969). The area is bounded by:

   712354 and 745000 East

   8008845 and 8064185 North

3. Western and Northern parts: the remainder of the study area which is not geologically mapped lying to the east or north of the central part, respectively.

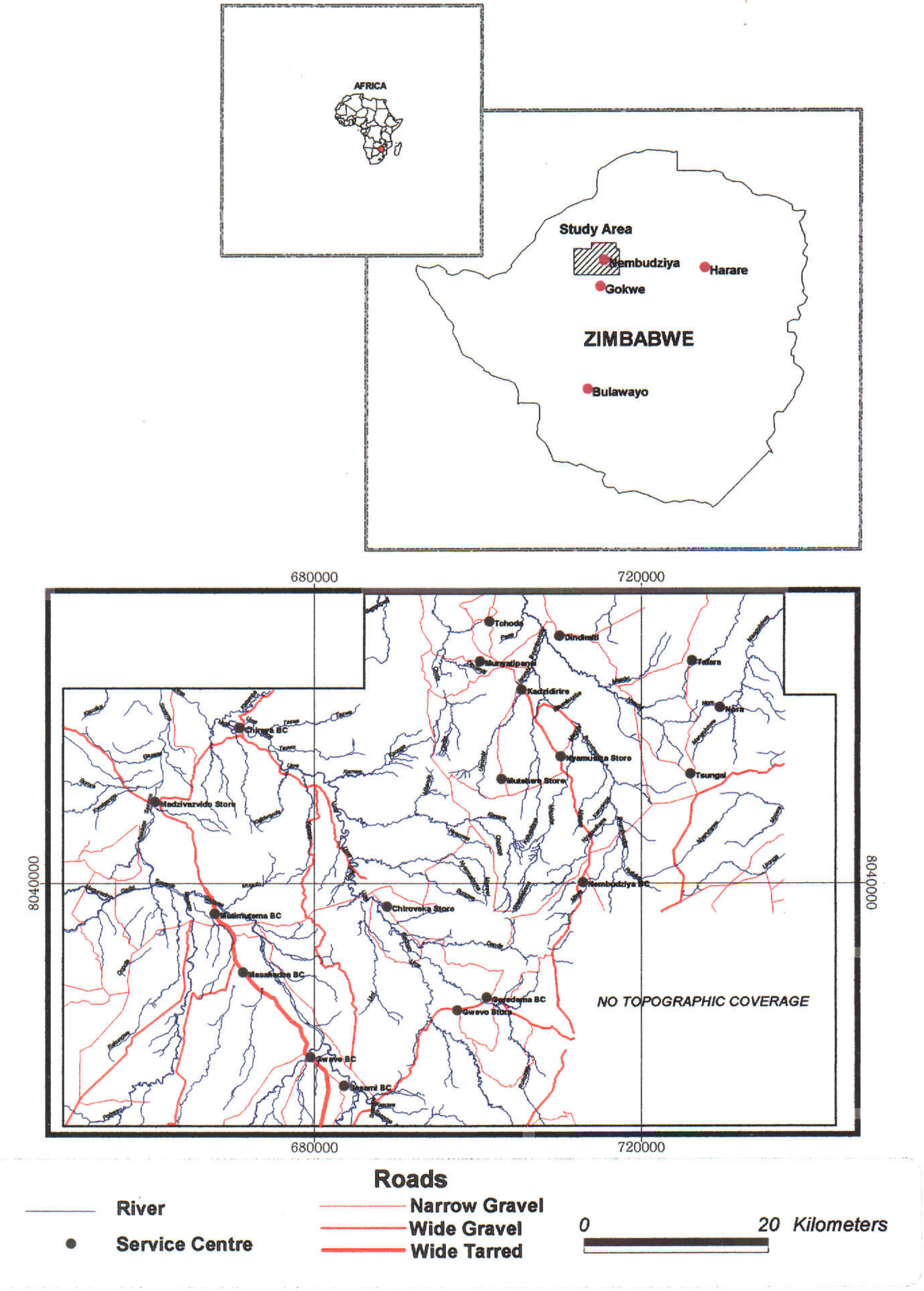


Figure 2.1: Location of the study area. The grid is UTM (Zone 35).

The main service centres in the area are Nembudziya Mission, Chireya Mission and Sesami Mission, but relatively higher order goods may only be obtained from Gokwe Town (Gokwe South District), some 42 km to the south of Nembudziya (Fig. 2.1). The area was sparsely populated prior to a major resettlement drive in the mid 1960s that followed successful tsetse control programs in the previously tsetse fly-infested area.

2.2 Relief

The study area lies within the Sanyati-Sengwa Basin of the Zambezi Valley Geomorphic Province (Lister 1987). The relief is determined to a large extent by resistance of local rock types to weathering, with the Batoka Basalt acting as a protective capping to underlying rocks (Sutton 1979; Ait-Kaci Ahmed *in prep*). Figure 2.2 shows the topographic contour map of the study area and a NW-SE topographic section. The contour map was constructed from Spline interpolation of values of spot heights taken from 1:50 000 topographic maps of the Surveyor General, Zimbabwe. The topographic peak near point A on the section corresponds to the basalt-capped Chinwavaenzi Range of the northern verge of the Mafungabusi Plateau and is up to 1140m in altitude. Along the line of section, the topography dips gently to the NW across the Lower Karoo sediments. The gentle slope is interrupted by a small upland made up of tectonically uplifted Escarpment Formation rocks. To the east of the line of section, the relief shaped by Upper Karoo sediments attains altitude of around 850m where not capped by basalt but rises appreciably higher at basalt capped hills such as Kadomo, Nyamuroro and Mumha (Ait-Kaci Ahmed *in prep*).

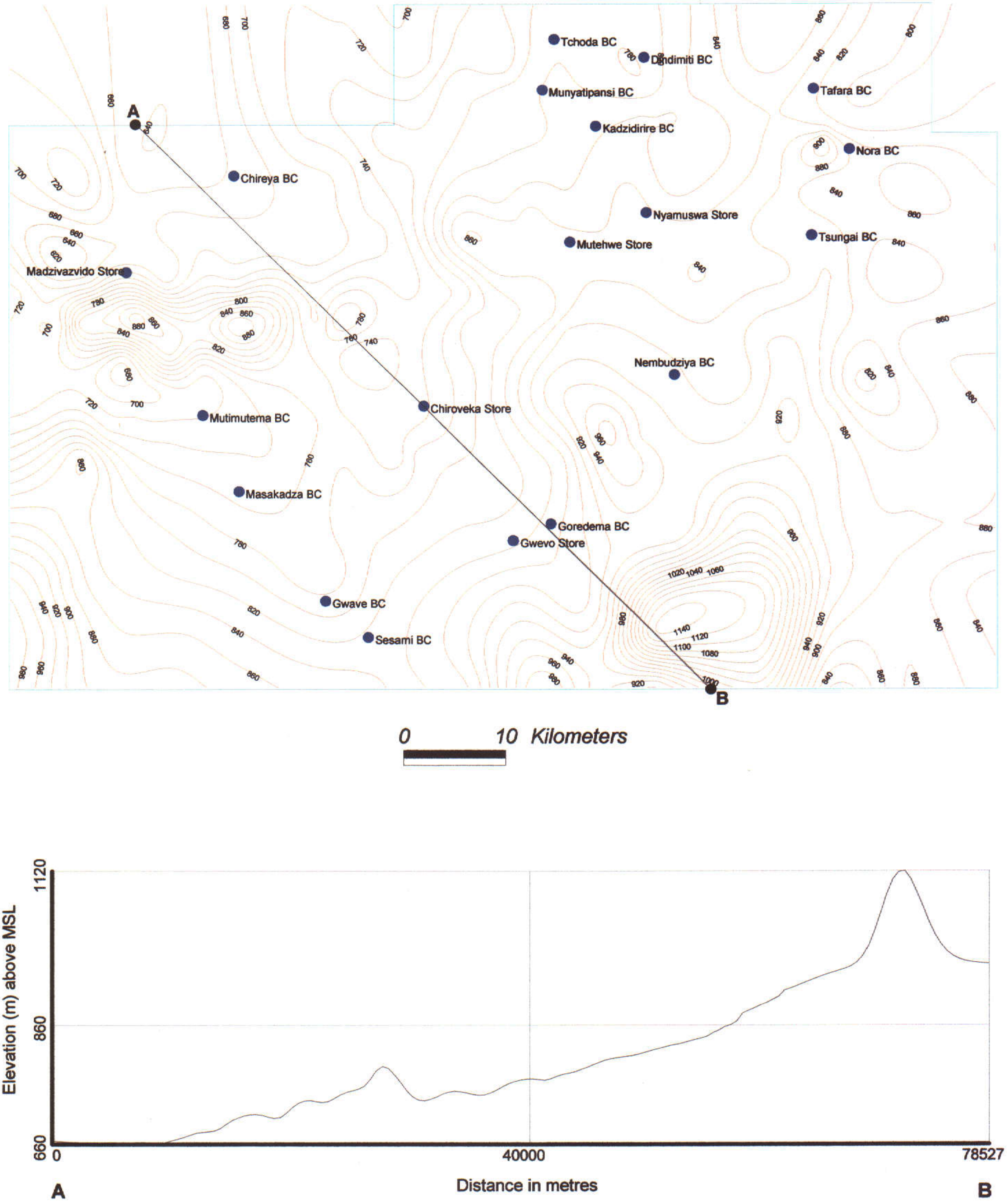


Figure 2.2: Topography of the study area.Top: topographic contours in metres above MSL and, bottom: topographic section along line AB, vertical exageration 50X.

2.3 Climate

Gokwe has a warm to hot climate, with a mean annual temperature of 23°C. The hottest month is October, with temperatures up to 46°C and a mean maximum of 34°C. Rains fall from November to April, registering an annual rainfall of 700mm, with January being the wettest month. The area experiences two seasons, a mild to warm dry season (May to October) and a hot wet season (November to May).

2.4 Geology

The central part of the study are is covered entirely by Karoo sedimentary sequences as mapped by Ait-Kaci Ahmed (*in prep.)*, while the eastern part, mapped by Leyshon (1969) consists of granites and gneisses in addition to Karoo rocks. The respective geological maps are shown separately in Figure 2.3 and Figure 2.5, with no attempt to join them because of obvious differences in mapping detail between the two. Throughout this thesis, the maps are treated as separate entities and, because of its greater lithological detail, the map of Ait-Kaci Ahmed (*in prep.),* forms the basis of extensive discussions on the link between geology and fluoride distribution covered in Chapter 6.

2.4.1 Geology of the Central Part of the Study Area

The central part of the study area consists of sedimentary rocks of the Karoo Supergroup. In this thesis, the latest stratigraphic nomenclature of Ait-Kaci Ahmed (*in prep.)* has been adopted, although observations of Bond (1955), Thompson (1981) and Lepper (1992) are also included. This is because the map of Ait-Kaci Ahmed (*in prep*), shown in Figure 2.3, covers the central part of the study area, which is also the key and largest part of the area,

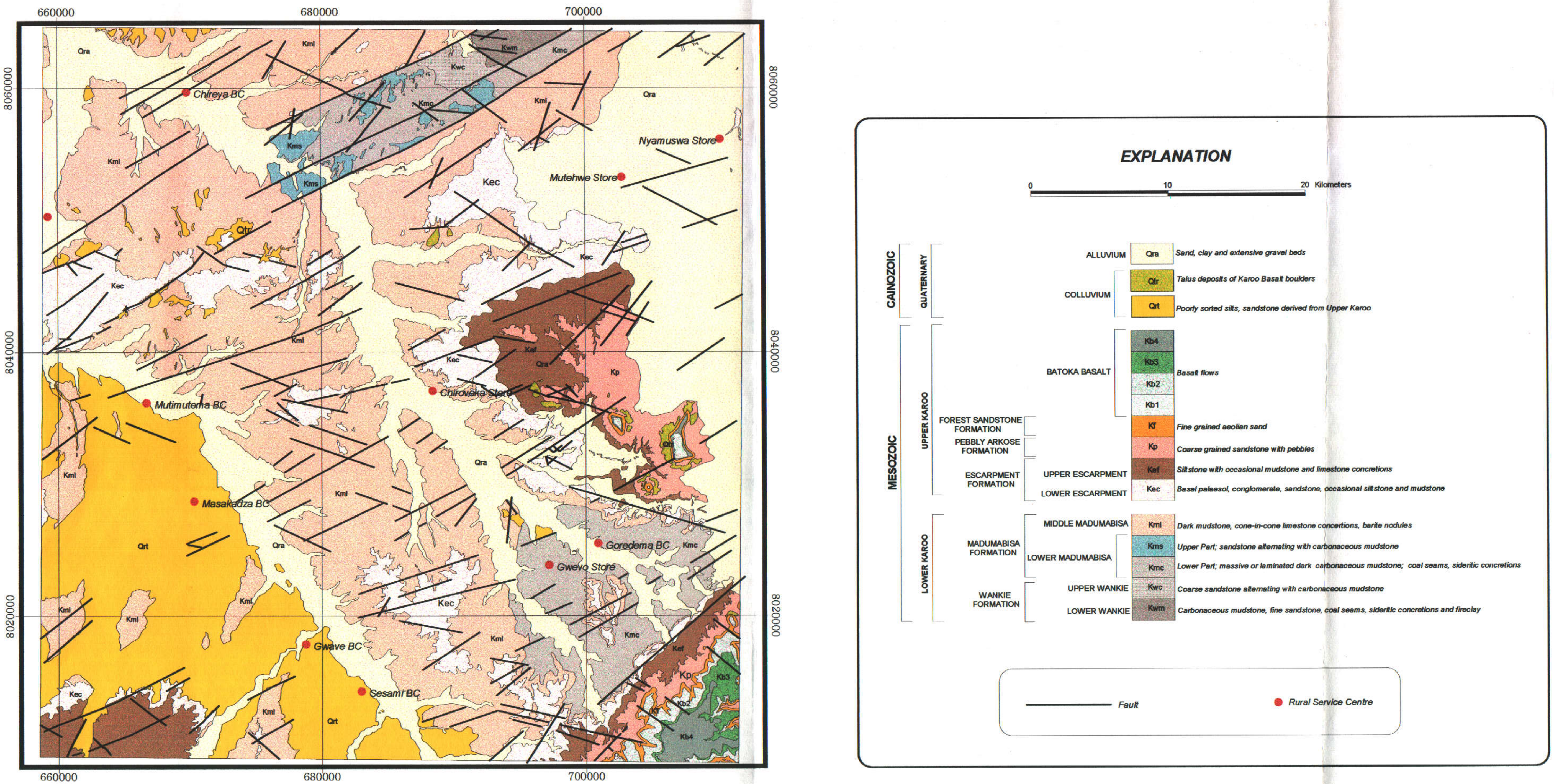


Figure 2.3: Geology of the central part of the study area. Mapped by Ait-Kaci Ahmed (in prep), and compiled and digitised by Mamuse (this thesis). The grid is UTM (zone 35)

while the rest are generally discontinuous reconnaissance works. The rocks of the Karoo Supergroup were deposited in the Sengwa Sub-basin of the Mid-Zambezi basin. The sub-basin is thought to be a synclinal structure inherited from a pre-Karoo floor consisting of the Neo-Proterozoic Sijaria Group at the centre, Palaeo-Proterozoic Piriwiri and Lomagundi rocks of the Magondi Belt towards the periphery and the Archaean Craton (granites, gneisses, metasediments, metavolcanics) in the northeast (Lepper 1992).

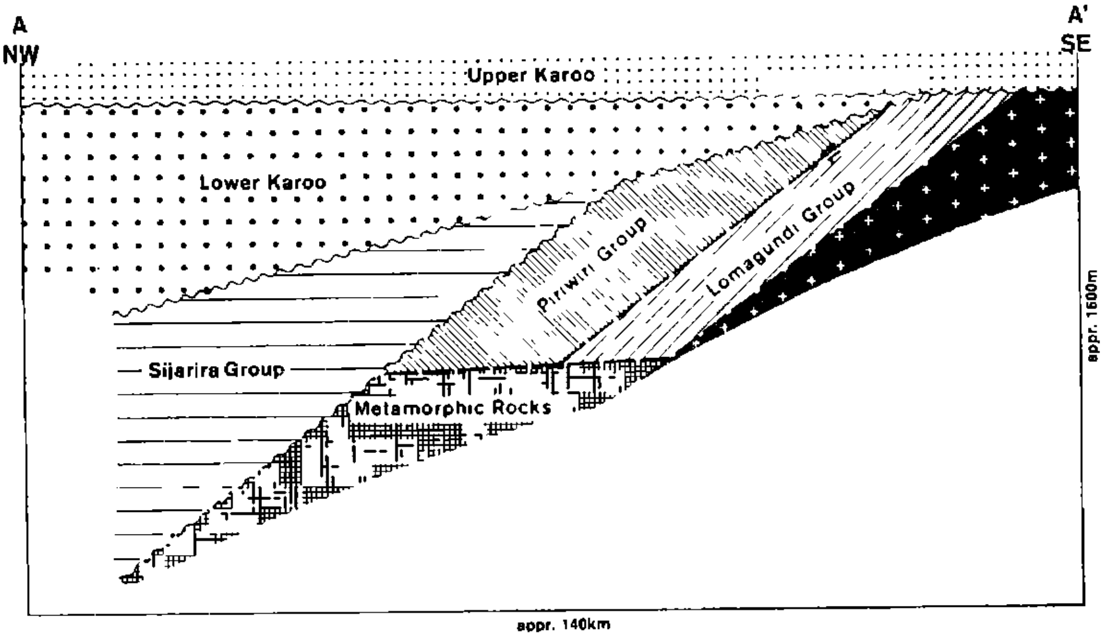


Figure 2.4: Diagrammatic section of the Sengwa sub-basin (from Lepper, 1992)

The Lower Karoo Group

The Karoo Supergroup consists of the Lower Karoo and Upper Karoo groups, which are separated by a regional erosional unconformity. As depicted in Figure 2.4, the Upper Karoo is sub-horizontal and rests on the Lower Karoo which dips and youngs to the northwest (Lepper 1992; Ait-Kaci Ahmed *in prep*). The Lower Karoo consists of the Dwyka, Wankie and Madumabisa Formations. The Wankie Formation is subdivided into three following members, namely Lower Wankie Member, Middle Wankie Member (previously Black Shale and Coal Group) and Upper Wankie Sandstone Member. In the case of the Madumabisa Formation, only the Middle Member and the Lower Member are encountered in the study area while the Upper Member is missing (Bond 1955; Ait-Kaci Ahmed *in prep*). The Escarpment, Pebbly Arkose, Forest Sandstone and the Batoka Basalt Formations constitute the Upper Karoo (Ait-Kaci Ahmed, *in prep*).

The **Dwyka Formation (Kds)**, considered to be the base of the Lower Karoo, consists of three alternating glacial facies, namely diamictites, varved clays and bedded fine sandstones and siltstones (Lepper 1992; Ait-Kaci Ahmed *in prep*). These deposits do not occur as a mappable unit in the study area.

Overlying the Dwyka is the 20 metre thick **Lower Wankie Member (Kwf)** consisting of coarse and fine ripple-marked sandstones with intercalations of carbonaceous mudstones. Interbedded between the Lower Wankie and Upper Wankie members is the 20 metre thick **Middle Wankie Member** comprising siltstones, fine sandstones, coal horizons, sideritic concretions and an iron-stained porcelanised cream-yellow mudstone (fireclay) (Ait-Kaci Ahmed, *in prep*).

The **Upper Wankie Sandstone (Kwc)** averages 30 metres in thickness and consists of poorly sorted white micaceous sandstones alternating with dark grey mudstones (Ait-Kaci Ahmed *in prep*) which may be referred to as lithic wacke (Lepper 1992). Trough cross bedding, planar cross bedding and laminations are some of the sedimentary structures identified in the wacke.

The lower part (Kmc) of the **Lower Madumabisa Member** consists of massive carbonaceous mudstones, grey shales and thin impure coal horizons with sideritic concretionary nodules up to 1m in diameter, which were deposited in a lacustrine environment (Lepper 1992; Ait-Kaci Ahmed *in prep*). In the study area, Member crops out to the north of Mutehwe and Chireya Mission, and around Goredema along the Kaongo and Ume rivers. It occasionally contains gypsum layers. The upper part of the Member, K^{5b}, comprises a basal microconglomerate composed of angular quartz clasts which grades into grey shales alternating with micaceous sandstones (Ait-Kaci Ahmed *in prep*). A massive coarse arkosic wacke similar to that of the Upper Wankie Sandstone is also considered a component of Kmc and has been previously called the Ridge Sandstone (Lepper 1992; Ait-Kaci Ahmed *in prep*).

According to Bond (1955) and Ait-Kaci Ahmed (*in prep*) the **Middle Madumabisa Member (Kml)** is commonly recognisable in the field by the disappearance of coal and the appearance of limestone, with its base containing limestone nodules of up to 1m in diameter. The member ranges in thickness from 0-90m (Lepper 1992) but occasionally it may be up to 140m thick (Ait-Kaci Ahmed *in prep*). The lower part generally consists of grey-green mudstone and marlstone, micritic concretions and cone-in-cone calcareous concretions, while the upper part comprises khaki mudstones with relatively few concretions (Bond 1955; Ait-Kaci Ahmed *in prep*). **The Upper Member**, which does not occur in the study area, will not be discussed here.

The Upper Karoo Group

At the base of the group is the **Escarpment Formation** which is composed of two members: the Lower Member (Kec) (gritty sandstones with lenses of cobbles, and pebbles) and the Upper Member (Kef) (siltstones and fine sandstones). Nyaruhwe, Kasavayo, Chiromo, Cherechere-Makari, Nyanende and Muratera hills are made up of the Kec. Southwards, the Kec thins out (down to 10m) and coarsens, but then gradually grades into Kef (Ait-Kaci Ahmed *in prep*). Kef is 30-40m thick in the Nyamuroro area and reaches 140m to the Southwest of Sessami Mission (Ait-Kaci Ahmed *in prep*).

The **Pebbly Arkose Formation (Kp)** 'is made up of well bedded arenaceous rocks, chiefly medium to coarse-grained arkoses, fine- to medium-grained red and pink sandstones, pebble sized conglomerates and impure fragmental limestones' (Sutton 1979, p. 176). However, according to Ait-Kaci Ahmed (*in prep*) in the mapped area the Formation, which is 80-100m thick, consists of quartz, chert and quartzite pebbles up to 2-3 cm across scattered in medium- to coarse-grained arkose with calcite cement.

The Forest Sandstone Formation (Kf) consists of friable, buff to white or pale pink, fine- to medium-grained sandstones consisting of subangular to rounded and partly frosted grains in a clay/silt matrix (Sutton 1979). Ait-Kaci Ahmed (*in prep*) also describes aeolian (well sorted, massive with local large scale cross-bedding) and fluvial beds (up to 3m thick; fining upwards from coarse sand to siltstone, with cross- and tabular-bedding). The Formation is about 100m thick at Kadomo and Nyamuroro hills and 80-90m at Chinwavaenzi Hill.

The **Batoka Basalts (Kb)** cap the Upper Karoo and are thought to have reached the surface by fissure eruption and at least four basaltic flows (Kb1-Kb4) each averaging 15 metres thick have been observed (Leyshon 1969; Sutton 1979; Ait-Kaci Ahmed *in prep*). According to the authors, interbedded sandstones, up to 10m thick, occur between basalt flows. The basalts are uniform, tough, fine- to medium-grained dark brown or black well jointed rocks which weather spheroidally to rounded boulders with a pitted skin (Leyshon 1969; Sutton 1979; Ait-Kaci Ahmed *in prep*).

Superficial Deposits

Unconsolidated regolith (elluvial, colluvial, alluvial) deposits, of probable Quaternary age, blanketing the Karoo stratigraphy are generally grouped as superficial deposits. In this context, Ait-Kaci Ahmed (*in prep*) recognises alluvium and two types of colluvial deposit as mappable superficial deposits in the study area. Along major watercourses such as Sesame, Ume and Kaonga rivers, alluvium occurs as an extensive (up to 2km from river course) unsorted mud sand and gravel deposit sufficiently thick to obscure the solid geology (Sutton 1979; Ait-Kaci Ahmed *in prep*). One type of colluvium consists of reddish loose sand with scattered gravels while the other type consists of colluvial basaltic boulders lying on top of one another with a little sandy matrix persisting upon the scarp of hills capped by Batoka Basalt (Sutton 1979; Ait-Kaci Ahmed *in prep*).

Geological Structure

According to Ait-Kaci Ahmed (*in prep*) there are pervasive, mostly pre-Upper Karoo, east and northeast trending faults (Fig. 1.2) exhibiting a few metres of normal throw in the study area. Another striking feature is the extensive erosional unconformity separating the Upper and Lower Karoo groups. Columnar and jointing is also common in the Batoka Basalt and it is this jointing that enhances spheroidal weathering of the basalts.

2.4.2 Geology of the Eastern Part of the Study Area

Granites and gneisses occur in the east of the study area (Fig 2.5), part of the map of Leyshon (1969). Leyshon (1969) named the igneous rocks 'The north-western granites and gneisses' with respect to his full map, describing them as a group of granitic and gneissic inliers that emerge through a cover of Karoo rocks.

The gneisses are considered to be part of the Archaean Basement and consist of a suite of gneissic, granitic, pegmatitic and schistose rocks (Nyuwe Gneiss) and dark fine-grained homogenous gneisses with ill-defined foliation (Dam and Wadzi Gneisses). The conspicuous granite mass in the area, called the Main Granite, is fine grained, massive and largely homogenous. The homogeneity is disturbed by the appearance of cross-cutting pegmatite veins, biotite pods, thin schlieren and feldspar phenocrysts in places.

Leyshon (1969) did not differentiate the Karoo rocks unconformably overlying the igneous rocks in the area. However, the Karoo rocks are likely to be similar to those mapped in the central part of the area by Ait-Kaci Ahmed (*in prep*). The Batoka Basalts encountered in the central part also continue into this, the eastern part of the study area and are similar to those of Ait-Kaci Ahmed (*in prep*).

2.5 Hydrogeology

2.5.1 Drainage

The drainage pattern of the area is depicted in Figure 2.1. The area is drained by the Ume and Sesame rivers and their tributaries. The Ume and its minor tributary the Kaonga originate in the Mafungabusi Plateau to the southeast of the study area. In the northwest corner, just northeast of Chireya Mission, the Ume is joined by its major tributary the Sesame which originates 5km east of Gokwe. The Sesame has a much larger catchment area than that of the Upper Ume. The Tari, Gwave, Dzire, and Pohwe among numerous other tributaries, join the left bank of the Sesame.

2.5.2 Groundwater

Figure 2.6 shows water level contours and a section of the groundwater surface through the line AB. The groundwater surface largely mirrors the topographic surface shown in Figure 2.2. This means that the groundwater flow direction in plan view will generally be parallel to the surface flow direction in the rivers. Three aspects of the data used in constructing the water level contour map (Fig. 2.6) must be pointed out: (1) the contour map was constructed (by Spline interpolation) from a limited number of water sources from which water levels could be obtained (see Appendix 1); (2) most of the water level data were measured in the course of study, but some were obtained from the work of ZINWA performed several years earlier; and (3) the water level contour map cannot be classified more precisely as a water table map, piezometric map or potentiometric map

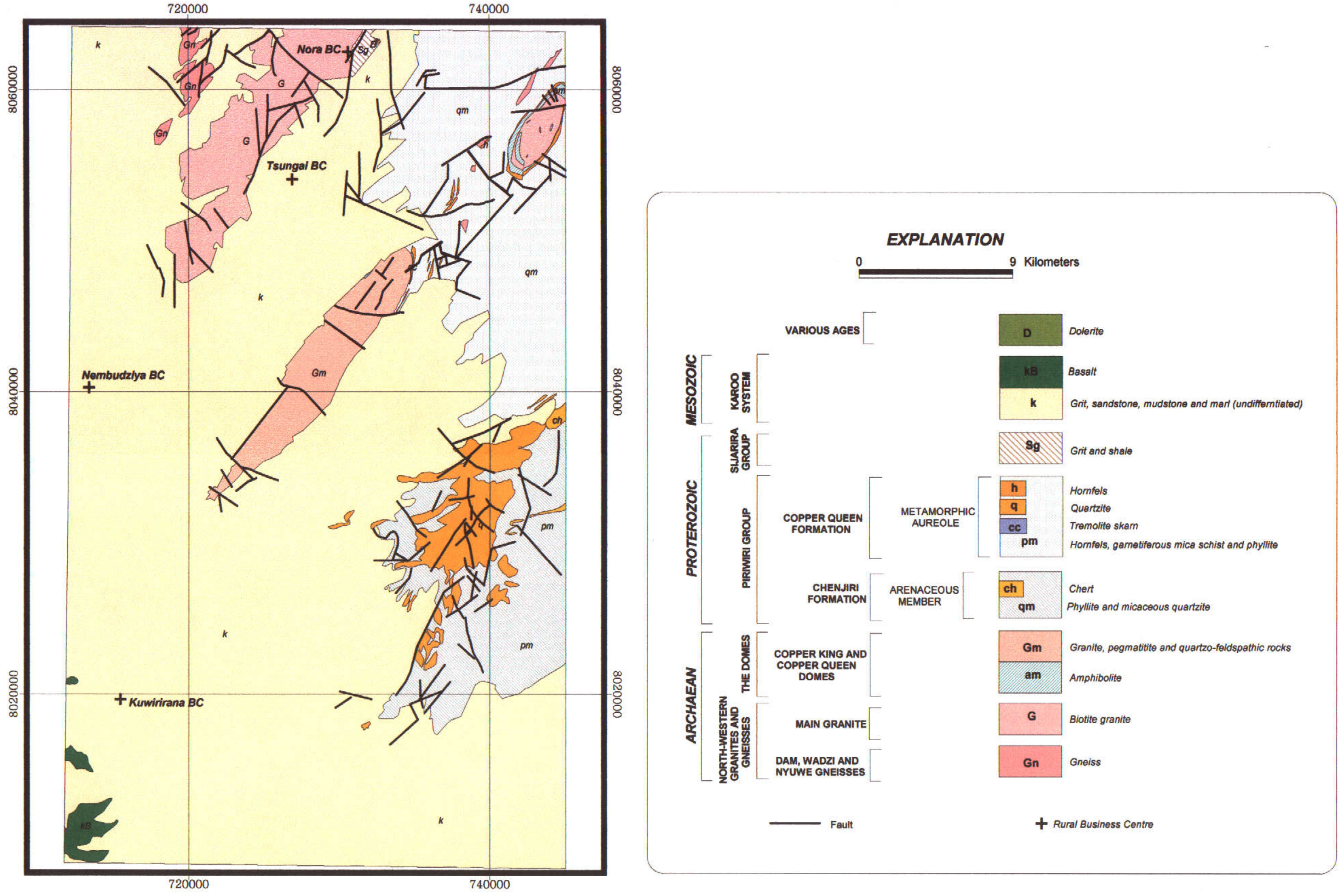


Figure 2.5: Geological map of the eastern part of the study area. The geology was mapped by Leyshon (1969) and degitised by Mamuse (this thesis). The grid is UTM (Zone 35).

Figure 2.6: Water Levels of the study area. Top: water level contours in metres above MSL and, bottom: water levels surface profile along line AB, vertical exageration 50X.

because full details of well construction and aquifer geometry were not known at the time of this investigation. It is likely that all the three possible types of ground water levels are included in the data and thus the map is a generalised 'water level contour map'.

The gross hydrogeological characteristics of the lithologic units in the study area are presented below.

Superficial Deposits

These deposits are particularly well developed along the Ume, Sesame and Munyati rivers where they form a marginal zone along the streams and up to 2km wide and 30 m thick. Because they are directly recharged from streambed infiltration, the deposits generally provide water of acceptable quality but quantities depend on the local clay content of the deposits (Ait-Kaci Ahmed *in prep*).

Batoka Basalts

The hydraulic properties of this lithological unit are controlled by secondary permeability emanating from joints and fractures, intergranular permeability, weathering zones in the basalts, and the local characteristics of the interbasaltic sandstones, and those of the underlying Forest Sandstone. According to INTERCONSULT^{AS} (1985), the groundwater from this aquifer normally has TDS below 1000 mg/L and does not contain excessive fluoride, although Magalela (1997) suggested that the fluoride contamination in groundwaters in the area may be associated with the basalts.

Forest Sandstone, Pebbly Arkose and Escarpment Formations

In the area of study, these formations generally bear insignificant groundwater resources because they are commonly located on elevated ground around basalt-capped plateaux and lose water through lateral drainage (INTERCONSULT^{AS} 1985; Ait-Kaci Ahmed *in prep.*). However, the Lower Member of the Escarpment Formation resting on an aquiclude (Madumabisa Mudstone) and below three (albeit minor) potential Upper Karoo aquifers, is likely to represent an important regional aquifer (INTERCONSULT^{AS} 1985; Ait-Kaci Ahmed *in prep.*). For example, on the wide escarpment plateaux of Nyaruhwe, Kasavayo and both sides of Kamwa River, the Member provides water from wells dug through the sandstone to the Madumabisa mudstone (Ait-Kaci Ahmed *in prep)*. Outside the study area where the Forest Sandstone is topographically low, it is known to be an important confined regional aquifer.

Madumabisa Mudstone

In the area of study, the Madumabisa Mudstone generally represents a regional aquiclude and acts as an upper confining layer for the Lower Karoo aquifer. Elsewhere, such as in Omay and in Binga Districts (to the north and west of the study area, respectively) sand intercalations in the mudstone are locally important groundwater bearing horizons (INTERCONSULT^{AS} 1985).

The Wankie and Dwyka Formations

The members of the Wankie Formation may be considered, for hydrogeology purposes, to form a single aquifer, the Lower Karoo Aquifer. This is justified because in the area of study, the Middle Member is either very thin (generally) or missing (in the east), and because of lithological (and hydrogeological) continuity between the Dwyka Formation and the Lower Wankie Member (Ait-Kaci Ahmed *in prep.*).

The Lower Karoo Aquifer (LKA) is widely distributed, has a thickness of 150-200m and generally possesses high primary porosity and permeability, making it an important regional aquifer (INTERCONSULT^{AS} 1985; Ait-Kaci Ahmed *in prep.*). Field evidence suggests that for most wells that penetrate the confined LKA substantially, the potentiometric surface lies at an elevation around 840-850m. Artesian flow therefore occurs in such wells where their collar elevation is below the elevation of the potentiometric surface (Ait-Kaci Ahmed *in prep.*). The major recharge for the LKA occurs in Sanyati to the east where it outcrops along the Mudzongwe and Munyati Rivers (Ait-Kaci Ahmed *in prep.*).

Lower Karoo Aquifer water is, however, of generally unacceptable quality because of excessive fluoride, chloride and of hydrogen sulphide odour (INTERCONSULT^{AS} 1985; Ait-Kaci Ahmed *in prep.*). Ait-Kaci Ahmed (*in prep.*) speculates that the fluoride concentrations may decrease eastwards as the Middle Wankie Member thins out. East of Munyati River (east of the study area) where the member is missing, water is of good quality and no cases of dental mottling are known.

Granites and Gneisses

In granites and gneisses groundwater occurrence is associated with porosities and permeabilities that are developed through jointing, fracturing and weathering of the rock bodies. In the study area, the gneisses and granites are pervasively faulted, fractured and weathered (Fig. 2.5). This suggests that reliable groundwater supply may exist in these rocks in the study area.

3

FLUORINE IN THE ENVIRONMENT

3.1 THE GEOCHEMISTRY OF FLUORINE

Fluorine consists of a single isotope of mass number 19 (isotopic mass 18.998) which because of its extreme electronegativity, rarely occurs in the elemental state but rather as the fluoride anion, F^-. Fluoride is a common constituent of rocks, soils and waters with rocks being the primary reservoir and ultimate source. It is estimated that crustal rocks contain an average of 300 ppm F, soils 200 ppm, river water 0.2 ppm, groundwaters 0.1-8.7 ppm and seawater 1.4 ppm (Bell 1998; Ming-Ho 2000). Fluorine is both a beneficial element and a potent environmental pollutant if present in excess amounts (Underwood 1980; Moynahan 1980; Mills 1996; Cerklewski 1997; Sinha et al. 2000).

In this section, some of the primary factors influencing the distribution of fluorine and the role it plays in some geochemical processes are discussed.

3.1.1 Fluorine Abundance in Rock-forming Minerals

Fluorine occurs in both rock-forming and accessory minerals, with accessory minerals accounting for 60% of all the fluorine minerals (Goldschmidt 1962, Koritnig 1978). It occurs as an essential constituent in many accessory minerals (such as villiaumite, cryolite, carobbiite and hieratite) but in only two rock-forming minerals (fluorite and topaz). Koritnig (1978) divided the remainder of the F-bearing minerals, in which fluorine occurs as an isomophous replacement in the OH position, into:

1. minerals in which the fluorine content is in the OH position as a constituent of a mixed crystal varying from the pure OH to the pure F-end member (i.e. apatite)
2. minerals in which fluorine is contained only in relatively small amounts, camouflaged in the OH^-, rarely in the O^{2-} position.

According to Koritnig (1978), the amount of fluorine in minerals in which it occurs as an isomorphous replacement is controlled by:

1. the amount of fluorine available in the rock-forming environment;
2. the physical properties of the OH^- (or the O^-) ion. The ionic sizes of the F^-, OH^-, and O^- ions are very similar such that one would expect easy substitution but since these ions have other very different properties (such as polarisability and electronegativity) this is not so. Rather it is the coordination and kind of ligands of the OH site that control the degree of replacement; and
3. in the case of micas and chlorites, O-fugacity of the environment.

3.1.2 Fluorine Abundance in Igneous Rocks

The mean F content in intermediate rocks is 400 ppm and in more acidic rocks it is 800 ppm, suggesting a general positive correlation between F^- and SiO_2 content of rocks (Goldschmidt 1962, Koritnig 1978). However, this apparent correlation does not extend to alkalic rocks which in general have a lower SiO_2 than acidic rocks, yet have the highest F-content (mean 1 000 ppm). Ultramafic rocks, with an average of 20ppm F contain the least F of all magmatic rocks, with phlogopite being the main carrier of fluorine (Koritnig 1978). Fluorapatite, biotite, phlogopite, pyrochlore, chondrite, rare earth minerals, sellanite and fluorite are the main F-bearing compounds in carbonatites (Day 1963, Koritnig 1978). Day (1963) suggested that much of the fluorine in igneous rocks is contained in the fluorapatite $(Ca_5(PO_4)_3F$, which in pure state carries 3.77%F. He however pointed out that the fluorine content is less because most apatites are not pure and have some replacement of F^- and OH^-.

It has also been suggested that plutonic rocks generally have higher mean fluorine contents than their extrusive equivalents, e.g. gabbro/basalt, 420/210; granite/rhyolite, 810/480 ppm F, although exceptions exist (Koritnig 1978).

3.1.3 Behaviour of Fluorine in Magmatic Processes

Behaviour During Crystallisation and Differentiation of Magmas

Fluorine tends to accumulate during the magmatic crystalisation and differentiation of magma and concentrates in residual magmas because the main rock-forming minerals do not accept significant amounts of fluorine in their lattices (Goldschmidt 1962, Koritnig 1978). Koritnig (1978) further pointed out that the following factors contribute to the relative enrichment of residual magma in fluorine:

- In the late crystallisation stages fluorine is able to enter OH-bearing minerals in structural positions of OH, but the amount of this fluorine is limited so that the residual magma is still further enriched in fluorine.

- HF is more soluble than water in silicate melts and thus will be accumulated to a higher degree in residual melts.

- With increasing alkalinity, the separation of fluorine into the gaseous phase decreases, causing fluorine enrichment in the melt.

Pegmatites

In pegmatites, fluorine occurs mostly in apatite, topaz, Li-micas, tourmaline, phosphates, carbonates and fluorite, most of which are formed during the pneumatolitic stage of pegmatite formation (Goldschmidt 1962, Koritnig 1978). Goldschmidt (1962) suggested that fluorine might be of major importance in the migration of volatile compounds in cassiterite-type pneutomatolytic mineralisation expressed by the following equation:

$$SnF_4 + 2H_2O = SnO_2 + 4HF$$

Goldschmidt (1962) further hypothesised that the HF may be responsible for the metamorphism of granite rocks into greissen, a mixture of quartz, highly fluorine bearing micas, and topaz, containing fluorine of the order of 1% by weight Goldschmidt (1962) further suggested that fluorine also tends to concentrate in contact metamorphism-related pneumatolytic deposits such as where limestones are transformed into mixtures of fluorite, magnetite and helvine (a berylium sulphide silicate) and contact zones of granites where fluorite zones commonly develop.

Hydrothermal Fluids

Fluorine that cannot be accommodated in crystalline phases during crystallisation and differentiation of magmas is accumulated in hydrothermal solutions which may form hydrothermal fluorite or react with previously crystallised minerals to form greissen (Bazarov et al., cited in Koritnig 1978; Schneiderhohn, cited in Koritnig 1978). Such fluorine is nearly always CaF_2 and in some cases leads to the accumulation of economic deposits of fluorite, although much fluorite may emanate from solutions in sedimentary rocks without any magmatic origin (Goldschmidt 1962). It is further noted that fluorine-poor hydrothermal fluids can leach fluorine out of the country rocks, as controlled by mineral solubility or ion exchange equilibria (Koritnig 1978)

According to Koritnig (1978), fluorite is the most abundant fluorine mineral in the hydrothermal cycle and it commonly forms fluorite veins and is usually associated with sulphide ores. The occurrence of sellaite (MgF_2) has been reported in a low temperature fluorite vein along with barites and traces of sulphides (Koritnig 1978).

3.1.4 Fluorine Abundance in Metamorphic Rocks

According to Koritnig (1978), available data on the occurrence of fluorine in metamorphic rocks are scant and largely restricted to skarns and metasomatism around granitic plutons, and the following generalizations have been made:

- Around greisenised granites, fluorine is contained in topaz, lithionite, zinnwaldite and fluorite.

- In common regional metamorphic rocks, fluorine mainly occurs in the OH bearing minerals, such as micas, chlorites and amphiboles.
- In skarns, fluorine occurs in amphiboles (tremolite, actinolite and anthophyllite), humite group minerals and vesuvianite.

3.1.5 Fluorine in Weathering Processes

The fluorine content of soils varies widely but averages 200 ppm (0.02%), a value lower than the average fluorine content in the lithosphere indicating that more F is extracted from soils during rock decomposition than is introduced from the atmosphere (Vinogradov 1959; Day 1963). The fluorine content of soils is constrained by the apatite (fluorapartite) content, possibly the most stable F-bearing component in soils (Day 1963; Koritnig 1978). Vinogradov (1959) suggested that of the fluorine is introduced into the soils by the decomposition of fluorapatite and as a result of the substitution of F from circulating groundwaters or from the air for OH^-, Cl^- and CO_3^{2-} in the phosphate rocks. Generally, the major part of the fluorine in soils is contained in the fine fraction of the soil (Vinogradov 1959).

For clays and argillaceous rocks, micaceous minerals are a more important contributor to fluoride content than apatite, with 80-90% of the fluorine contained in muscovite, illite and other mica-group minerals (Vinogradov 1959; Day 1963; Koritnig 1978) The remainder is contained in montimorillonite, kaolinite and apatite.

3.1.6 Fluorine Abundance in Natural Waters

Most waters contain fluoride at least in trace amounts. The primary reservoir source and ultimate source of fluorine and other elements in water are the rocks of the Earth's crust (Owen & Jones 1995). While the dominant species of fluoride in water is free dissolved fluoride, at low pH the species HF may be stabilised and is actually dominant at pH below 3.5 (Hem 1985). Edmunds & Smeldley (1996) and Bell (1998) noted that concentrations of F in water are limited by the solubility of F-bearing minerals, principally fluorite, and apatite, and to a lesser extent fluoride-substituted minerals like amphibole, mica, titanite and pyroxene. They explained that solubility is limited in the presence of calcium and, consequently, high concentrations of fluoride are likely to occur in groundwater in calcium-poor aquifers and in areas where fluoride-bearing minerals are common. One of the earlier investigators on the F and Ca relationships in waters was Handa (1975) who demonstrated the negative correlation between F and Ca concentrations in Indian groundwater. Fluoride concentration is known to increase in groundwaters where cation exchange of sodium for calcium (and magnesium) takes place, and in thermal high pH waters (Edmunds and Smedley 1996; Bell 1998). The extent of this replacement may be estimated by the sodium adsorption ratio (SAR), expressed as:

$$\mathrm{SAR} = \mathrm{Na}/\sqrt{[(\mathrm{Ca} + \mathrm{Mg})/2]},$$

where Na, Ca and Mg represent the respective ionic concentrations in milliequivallents per litre (Davies and DeWiest 1966).

Groundwater and Hot Springs

The fluoride content of groundwater is controlled by the types of rocks and soils through which the water circulates before leaching out and dissolving in the groundwater (Koritnig 1978). For hot springs, Koritnig (1978) suggested that the fluoride content (0.15-8.0 ppm) increases with temperature of the springs which typically ranges from 30°C-95°C for the springs of the Saga Pref., Japan.

Rivers, Lakes and Oceans

The fluoride content of surface water depends on the fluoride content of the groundwater feeding a particular stream and on the amounts of precipitation and runoff, and it is generally higher during dry periods (Koritnig 1978). In general rivers and lakes contain less than 0.5mg/L fluoride although concentrations as high as 95mg/L have been recorded in Tanzania where the soil is rich in fluoride containing minerals (WHO 2000). Koritnig (1978) cited the use of chemical fertilisers as a significant contributor to fluoride content in soils. In Kenya, Gaciri and Davies (1993) recorded fluoride contents of over 2000mm/L in some lake waters.

The mean concentration of fluoride in ocean water is in the range 0.03-1.35 ppm (Koritnig 1978).

Rainwater

Marine aerosols may be the major source of fluorine in rainwater (Koritnig 1978). In areas of the USA remote from industry and dense population, fluoride content in rainwater ranges from 0-0.004 ppm. In the vicinity of cities and industrial areas the fluoride content of rainwater may be as high as 1 ppm (average 0.29 ppm) areas (Koritnig 1978).

It has been reported that in Tennessee, rainwater contributed an average of 2 g of fluorine per 100 m^2 of soil per year (Vinogradov 1959).

3.1.7 Fluorine in the Atmosphere

Most estimates put normal atmospheric fluorine content in the range 0.01μg/m^3 to 1.90 μg/m^3 (Koritnig 1978; WHO 1996; 2000). In industrial areas, fluorine content in the air is up to 36 μg/m^3 (Koritnig 1978). Acidic volcanic fumes, which contain a large amount of HF, constitute a significant source of F in the biosphere and this explains why areas of recent volcanism have waters, rocks and soils with elevated F-contents (Vinogradov 1959). Such areas occur in Indonesia, and around Vesuvius, Katmai, Hekla, Iceland, Kilauea and in the Great East African Rift Valley System, which are generally associated with fluorosis affecting animals and people particularly after an eruption (Vinogradov 1959).

In parts of rural China, the burning of high-fluoride coal and the baking of bricks and tiles from high fluoride mud pollutes the indoor and outdoor environments considerably through the emission of gaseous and aerosol fluoride (Chen 1991; Ando et al. 2001).

3.1.8 Fluorine Abundance in Sedimentary Rocks

It has been suggested that fluorine may be more abundant in sediments of marine origin than those originating from non-marine environments (Koritnig 1978; Edmunds 1995). In the present-day sedimentary cycle, calcium carbonate precipitation is probably the main process of fluoride removal from seawater and next in importance is fluorine incorporation into calcium phosphate (Koritnig 1978).

The major fluoride bearing minerals in carbonate rocks are fluorite, apatite and clay minerals; in rock salt fluorine occurs in apatite, fluorine phosphates, isokite ($CaMgFPO_4$) and wagnerite ($MgFPO_4$) and almost all the fluorine in marine anhydrite is contained in fluorite (Koritnig 1978).

Although fluorine is the most abundant halogen in sedimentary rocks (Kortinig 1978), it is a relatively rare element in these rocks except where concentrated in specific areas of mineralisation (Edmunds 1995). Such areas of mineralisation include shale-hosted Pb, Zn and Ba epigenetic deposits which form from brines associated with dewatering of sedimentary basins, and in which associated minerals include fluorite (Maynard 1991).
From coal washing experiments, Schultz et al. (1973) reported that fluorine appeared to be associated with the mineral matter (rather than the organic matter) of the coal. Correlations between fluorine and phosphorous contents in analyses of coals from England and the Western USA suggested that fluorapatite was the mineral phase associated with fluorine in those coals (Bouska 1981).

3.2 FLUORINE AND HUMAN HEALTH

Insufficient, excessive or unbalanced dietary supply of certain inorganic elements can adversely affect human health. In societies where nutrition is largely autochthonous, such as in rural communities in developing countries, specific health conditions can be linked directly to anomalies in the distribution of certain elements in the environment (Moynahan 1980; Mills 1996; Plant et al. 1998). These anomalies are inconsequential in developed countries where varied diets (with food items sourced from different regions) and dietary supplements can provide adequate element levels, thus eroding the direct linkage between environmental chemistry and health.

Fluorine is one element whose environmental concentration can produce noticeable adverse effects on human health. Chronic fluoride toxicity, which commonly manifests as fluorosis, is probably one of the most widespread endemic health problems associated with natural geochemistry (Belyakova & Zhavoronkov, cited in WHO 2000).

3.2.1 The bioavailability of fluoride

The principal source of fluoride for humans is water but other important sources include food, beverages, dental products, fluoride supplements and infant formulas (Hodgson et al. 1971; NRC 1993; Cerklewski 1997; WHO 1996; 2000). On average, an adult body contains a total 2.6 g F (making F the second most abundant trace element after iron) and more than 95%-99% of this total is found in the bones and teeth (NRC 1993; Cerklewski 1997). The absorption of ingested fluoride does not involve active transport, but passive diffusion via the membrane channels from both the stomach and intestinal mucosa

(Cerklewski 1997; Ming-Ho 2000). High levels of gastric acidity favour fluoride absorption in the stomach whereas alkalinity decreases the absorption rate; absorption from the small intestine is non-pH dependent (Cerklewski 1997). In all, about 75-90% of the ingested fluoride is absorbed from the alimentary tract and the remaining 10-25% remains to be excreted in faeces (NRC 1993). It is estimated that of the fluoride absorbed by the young or middle-aged adult, 50% will be associated with calcified tissues within 24 hours and the remainder will be excreted in urine (NRC 1993). Renal clearance of fluoride is directly related to urinary pH and factors such as metabolic disorders and altitude of residence which affect urinary pH in turn affect the extent to which absorbed fluoride is retained in the body (Whitford 1989; Whitford & Pashley 1991).

The most efficient uptake of fluoride into bones and teeth occurs during childhood due to the existence of a large surface area provided by numerous and loosely organised bone crystallites and due to the very rapid skeletal development (Guo et al. 1988; NRC 1993). However, according to Den Besten & Crenshaw (1987) and Suckling et al. (1988) fluoride at sufficiently high concentrations might affect enamel at all stages of its formation. Young children who drink water containing 0.7-1.2 mg/L of fluoride consume about 0.5mg F per day or 0.04-0.07mg/kg of body weight per day (NRC 1993).

Calcium and magnesium are known to influence the bioavailability of fluoride by forming insoluble complexes with it, thus reducing its uptake into bone and teeth (Cerklewski 1997). The formation of the insoluble complex depends on the timing and chemical form of the fluoride; there is only minimal effect on intestinal fluoride absorption if the interfering cation is not in the same meal as the fluoride and monofluorophosphate is less affected by complexation than sodium fluoride (Spencer et al. (1975; 1978). Aluminium is the only other cation that has also been found to form an insoluble complex with fluoride (Cerklewski 1997).

Chloride is the only anion known to influence fluoride bioavailability. A low chloride diet increases fluoride retention by reducing fluoride urinary excretion by one third (Cerklewski 1997). Fats and proteins also have an influence on fluoride absorption and bioavailability: high dietary fat increases fluoride absorption by delaying gastric emptying time while high dietary protein increases fluoride absorption by a stimulation of gastric acidity which favours the formation of highly diffusible hydrogen fluoride (Cerklewski 1997). However, greater fluoride absorption by increasing protein intake is more than offset by a marked increase in urinary fluoride excretion resulting in a net decrease in fluoride bioavailability as estimated by fluoride intake into the bone (Cerklewski 1997).

3.2.2 The Biochemical Function of Fluoride

Skeletal Constituent

Calcium and phosphorus in the form of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, constitute the major crystalline material of mature bone and teeth. The formation of fluoroapatite, $Ca_{10}(PO_4)_{2-2x}F_{2x}$, by the substitution of fluoride for hydroxyl in the hydroxyapatite crystal structure promotes increased apatite crystal size, reduced crystal distortion and reduced solubility of the apatite crystal (Cerklewski 1997).

Metabolic Functions

Ming-Ho (2000) suggested that fluoride affects numerous other processes involving Ca in humans, including blood clotting, membrane permeability, nervous system functions and chlorinesterase. He added that many inhibitory effects of F in reactions involving Ca are due to the formation of CaF_2 as shown below:

$$[\text{Protein-Ca}] \leftrightarrow \text{Protein} + Ca^{2+}$$

$$Ca^{2+} + F^- \leftrightarrow [CaF] + F^- \leftrightarrow CaF_2$$

Cerklewski (1997) and Ming-Ho (2000) noted that as a metabolic inhibitor, fluoride affects various biological processes including fluoride-dependent inhibition on enzymes via the following mechanisms: (i) the removal of a metal cofactor such as Ca or Mg, (i) formation of complexes with metalloenzymes and (iii) binding to the free enzyme or to the complex substrate. They also suggested that fluoride also mediates by forming a magnesium-fluorophosphate complex in enzyme systems requiring magnesium.

Dental Caries Prevention

Organic acids produced from fermentable carbohydrates by bacteria in tooth plaque of the tooth enamel cause dissolution of enamel mineral resulting in tooth decay (dental caries) (Underwood 1980; Cercklewski 1997; Ming-Ho 2000). Fluoridation of water supplies has been widely accepted as a public health measure since fluoride is known to prevent dental carries in children (Underwood 1980; Moynahan 1980; NRC 1993; Mills 1996; Riley et al. 1999; Jones & Worthington 1999; Sinha et al. 2000; Hillier et al. 2000). At concentrations less than 0.5mg/l total F, dental carries may develop (Moyanahan, 1980; Edmunds & Smedley 1996; Konieczka et al. 2000). Fluoride's primary role in caries prevention is by a combination of inhibition of demineralisation (due to reduced solubility of the apatite structure) and increased remineralisation rate (fluoride stimulates apatite crystal growth and precipitation) (NRC 1993; Cerklewski 1997). It is further suggested that fluoride bound in dental plaque inhibits glycolysis, a process by which bacteria metabolises sugar to acid. It also inhibits the production of extracellullar polysaccharide required for plaque to adhere to smooth enamel surfaces (NRC 1993).

3.2.3 Manifestations of Endemic Fluorosis

Dental Fluorosis

Dental fluorosis refers to a 'hypomineralisation of enamel, characterised by greater surface and subsurface porosity than is found in normal enamel, and results from excessive fluoride reaching the tooth during developmental stages' (NRC 1993, p.22). This improper enamel crystallisation leads to defects ranging from barely discernible to severe brown staining, surface pitting and brittleness. The clinical signs of severe dental fluorosis (enamel pitting and obvious brown staining) follow the breakdown of the better-mineralised surface layers of enamel shortly after eruption, resulting in a variable uptake of mineral in the exposed hypomineralised subsurface lesions (Thylstrup 1983; Fejerskov et al. 1991). The authors further stated that the staining actually develops after tooth eruption, but only becomes obvious if porous enamel has formed before eruption. Richards et al. (1989) pointed out that surface enamel that exhibits fluorosis contains higher concentrations of fluoride than does normal enamel, and that the fluoride content increases with fluorosis severity. For example when drinking water contains fluoride up to 0.1mg/L, enamel contains an average of 1700 mg/L fluoride, and at concentrations of

5-7mg/L fluoride in drinking water, enamel contains an average of 4 800ppm fluoride (NRC 1993). A low unrinary pH caused by, for example, metabolic or respiratory disorders, diet, drugs and altitude of residence, reduces the renal clearance of fluoride and increases the likelihood of dental fluorosis (NRC 1993). Angmar-Mansson & Whitford (1990) further pointed out that living at high altitudes could disrupt amelogenesis and produce a condition clinically similar to dental fluorosis even in the absence of fluoride. A further complication is that malnutrition, metabolic disorders and the presence of other dietary trace elements can lead to diffuse symmetrical markings on the enamel that resemble fluorosis (NRC 1993).

Gedalia & Shapira (1989) pointed out that fluorosis is mainly a condition of permanent rather than primary teeth. They suggested that this could be due to the fact that the pre-eruption enamel maturation period, during which most enamel fluoride is deposited is longer for permanent teeth (4-5 years) than for primary teeth (1-2 years). However, it has been found that primary teeth can also be affected by fluorosis where fluoride ingestion is exceedingly high (Thylstrup 1978; Larsen et al. 1985; Mann et al. 1990).

Skeletal and Crippling Skeletal Fluorosis

According to WHO (1984, 1996) skeletal fluorosis, characterised by adverse changes in bone structure, can occur in people who regularly consume drinking water containing 3-6 mg/L of fluoride per litre. It is generally known that fluoride affects the bone in at least two ways: fluoride can replace hydroxyl ions in the hydroxyapatite lattice; and increased fluoride in plasma directly increases osteoblastic differentiation and activity (e.g. Smith & Hodge 1979; Jenkins 1990; Riggs et al. 1990; Hillier et al. 2000). USEPA (1985) suggested that the best predictor of the effects of fluoride upon the skeleton are the level of fluoride in bone, usually measured as the fluoride level in bone ash. Smith & Hodge (1979) and WHO (2000) distinguished two skeletal fluorosis stages, namely a pre-clinical stage characterised by slight increases in bone mass, and a clinical stage. They reported that bone ash from adults who have chronically consumed water with optimal fluoride concentration contains less than 1500 ppm fluoride and in pre-clinical stages this increases to between 3500 and 5500 ppm and is radiographically detectable. Skeletal fluorosis stage 1 is marked by bone ash fluoride concentrations of 6000-7000ppm and at 7500ppm-8000ppm, stages 2 and 3 occur (Smith & Hodge 1979). Clinically, stage 1 is characterised by stiffness or pain in the joints and some osteoscleosis of the pelvis and vertebral column. Symptoms of stages 2 and 3 include chronic joint pain, ligament calcification, osteosclerosis, osteoporosis of long bones, muscle wasting and neurological defects (Smith & Hodge 1979).

Crippling fluorosis results from gross excessive exposure to fluoride and was originally described in Danish cryolite workers who inhaled fluoride-containing dust for 10-20 years (Carnow & Conibear 1981; Cerklewski 1997). According to WHO (1984; 1996) and NRC (1993) fluoride concentrations above 10mg per litre of drinking water may lead to crippling skeletal fluorosis.

WHO (2000) noted that the actual fluoride level required to produce crippling skeletal fluorosis differs from region to region, as demonstrated by studies in Senegal (Brouwer et al. 1988) and the USA (Leone et al., cited in WHO 2000). In the US study, 237 individuals were X-rayed in 1943 and in 1953, half from Bartlett, Texas (with fluoride levels of 8mg/L in drinking water) and Cameron Texas (0.4mg/L fluoride). No evidence of crippling skeletal fluorosis was found in the individuals whose average residence times in their respective areas were 37 years and 38 years. Only an increased incidence of osteosclerosis (asymptomatic darkening of bone under the X-ray) was observed in the higher fluoride area. Brouwer et al. (1988) found that of the 42 individuals who had consumed drinking water with 7.4mg/L fluoride, 11 (26%) had developed skeletal fluorosis. This sharp difference may possibly be attributed to differences in local conditions such as diet and water consumption rates (WHO 2000).

Several studies have suggested that relatively low levels of fluoride in drinking water (1-4mg/L) may be associated with bone fracture (e.g. Sowers et al. 1991, Danielson et al. 1992). Other studies, however, have established only weak or no correlation between fluoride concentration in drinking water and the incidence of bone fracture (e.g. Madans et al. 1983; Cauley et al. 1995; Arnala et al., cited in WHO 2000; Hillier et al. 2000).

Other Health Effects of Fluoride on Humans

Effects of fluoride on non-skeletal tissues, such as effects on pregnancy outcomes and the immune system have been investigated. It has been suggested that available data on pregnancy outcomes are inconclusive (WHO 1996; 2000) and that fluoride may not produce hypersensitivity and other immunological effects on humans (NRC 1993, WHO 2000). In reviews of studies on the possible link between fluoride in drinking water and cancer rates among human populations, it has been concluded that there is inadequate evidence to suggest that fluoride is a carcinogen (NRC 1993; WHO 1996; 2000).

According to NRC (1993) renal excretion, the major route of inorganic fluoride excretion, makes the kidney a potential site for acute fluoride toxicity with toxic effects produced in animals at 50 mg/L fluoride in drinking water. NRC (1993) concluded that at the fluoride concentration recommended by EPA (4mg/L), kidney toxicity is unlikely while WHO (1996; 2000) pointed out that the data are too limited to permit any evaluation of possible increased sensitivity due to impaired kidney function. With regard to genotoxicity, it has been found that in mammalian cells *in vitro*, fluoride causes chromosomal aberrations and inhibits protein and DNA synthesis at concentrations of 10 mg/L or above. However, the normal concentration of fluoride in human plasma is 0.02-0.06 μg/mL, implying that the genetic effect of fluoride is of no concern for practical human exposure (NRC 1993; WHO 1996; 2000). It must however be mentioned that adverse effects of fluoride on reproduction, renal system, immune system, gastrointestinal system and in carcinogenicity have been positively established in animals (NRC 1993; WHO 1996; 2000).

The health effects of fluoride mentioned up to now may be termed 'chronic fluoride toxicity', that is, those effects resulting from long periods of exposure to relatively low fluoride levels. At relatively large doses of fluoride, 'acute effects' may result. To produce signs of acute fluoride intoxication, minimum oral doses of at least 1mg of fluoride per kg of body weight are required and such doses could be expected from water with a fluoride content of approximately 30 mg/L fluoride (Martin 1991; WHO 1996; 2000). Death in human adults may occur two to four hours after 5 g of sodium fluoride is ingested, with nausea, vomiting, and abdominal cramping as symptoms preceding coma and death (Martin 1991; Cerklewski 1997; Konieczka et al. 2000).

3.2.4 Fluoride Exposure

According to WHO (2000), drinking water is typically the largest single contributor to the daily fluoride intake although, in some situations, food, beverages (e.g. tea) air, dental products (such as toothpaste and mouthwash), infant formulas and fluoride supplements (NRC 1993; WHO 1996; 2000) may be significant sources of fluoride exposure.

Dean (1942) established that the optimal level of fluoride in drinking water is 1.0mg/L from which the USPHS set a temperature-related optimal range of 0.7-1.2 mg/L fluoride. WHO (1984) recommended a guideline value of 1.5mg/L fluoride in drinking water and while WHO (1996) maintained that there was no evidence to suggest that the value needed to be revised, it suggested that it is important to consider climatic conditions, volumes of water intake, and fluoride intake from other sources (such as food and air) in setting national standards for fluoride. Taking this into account, WHO (1996) suggested that 'as a rough approximation' in temperate areas, obvious dental fluorosis may occur at concentrations above 1.5-2mg/L fluoride in drinking water, and at lower concentrations in warmer climates where more water is consumed. WHO (1996) further suggested that skeletal fluorosis may develop from exposure to 3-6mg/ L fluoride in drinking water, and that at above 10mg/L fluoride, crippling skeletal fluorosis occurs.

The recommended maximum contaminant level (RMCL) for fluoride has been subject of debate. Several authors (e.g. Galagan 1953; Richards et al. 1967; Moller 1982) have long pointed out that the concentration at which fluoride causes dental fluorosis varies from country to country and that for tropical countries, the recommended levels should be set below those for temperate climates. Warnakulasuriya et al. (1992) reported that among people ingesting water containing less than 1.0 mg/L fluoride in Sri Lanka, 32% of children had mild forms of dental fluorosis and 9% severe forms. From this work it was recommended that the WHO upper limit for fluoride in drinking water in hot dry climates should be 0.8mg/L. Chen et al. (1988) in a large scale survey in China reported that dental fluorosis was detectable in 46% of the population consuming water with 1mg/L fluoride.

EPA (1985) set the RMCL for fluoride in drinking water at 4mg/L regardless of mean temperature arguing that this concentration was low enough to prevent crippling skeletal fluorosis although not protective against dental fluorosis, a 'purely cosmetic effect'. The reasoning was that even severe dental fluorosis is acceptable when compared to the costs of defluoridating many small towns' water supplies (NRC 1993). This infuriated sections of the community and the EPA tasked the National Research Council's (NRC) Committee on toxicology (COT) to review existing fluoride toxicity data and to determine whether the EPA's fluoride RMCL was appropriate. NRC (1993) concluded that the fluoride 4mg/L RMCL in drinking water was appropriate as an interim standard, noting that at that level a small percentage of the US population will exhibit moderate or even severe dental fluorosis. However other institutions and individuals rejected these findings. For example, Carton (1991, p.1) dismissed the EPA RMCL as 'a classic case of political interference with science' in which documents were falsified to protect a longstanding health policy. Even NRC (1993) noted that severe dental fluorosis is more than a cosmetic defect 'if enough fluorotic enamel is fractured and lost to cause pain, adversely affect food choices, and require complex dental treatment' (NRC 1993, p.182). Martin (1991, p.183) suggested rhetorically that dental fluorosis may be just the external symptom of a serious problem affecting more tissues and cells of the body, 'Is dental fluorosis an external sign of general cellular toxicity, unique only in its visibility, while less detectable effects occur in other tissues? Or are the ameloblasts-the cells that lay down the enamel as teeth grow inside the jaw-uniquely sensitive to fluoride?'

Table 3.1 summarises the presumed impact of various levels of fluoride on health as suggested by various researchers or organisations:

Proposing body/ researcher	Presumed effects at given fluoride concentration (mg/L) in drinking water					
	Dental caries	Optimal	RMCL	Objectionable Dental fluorosis	Skeletal fluorosis	Crippling fluorosis
Dean (1931, 1942)	<1.0	1.0		>2.0		
USPHS (1942)		1.0				
USPHS (1962)		0.7-1.2	1.4-2.4	>1.4		
EPA (1985)						>4.0
NRC (1993)						>4.0
WHO (1984, 1996, 2000)			1.5	>1.5	3-6	>10
Edmunds & Smeldley (1996)	0-0.5	0.5-1.5	1.5	1.5-4.0	4.0-10	>10
CSIR		>1.5			<3.5	

Table 3.1: Possible health effects of fluoride

Virtually all foods and beverages contain at least some traces of fluoride, with the highest concentrations in fish (0.1-30 mg/kg) and fish concentrates (up to 370 mg/kg) and tea (up to 400mg/kg) (WHO 1996; 2000). According to WHO (1996), vegetables and fruits normally have low levels of fluoride (0.1-0.4 mg/kg), with curly kale (up to 40 mg/kg fresh weight) and endive (0.3-2.8 mg/kg fresh weight) being among the most fluoriferous field-grown vegetables. Barley, rice, taro, yams and cassava have also been found to contain relatively high levels of fluoride (WHO 2000). The fluoride content of milk is generally low. It is about 0.02 mg/L in human breast milk and 0.02-0.05mg/L in cow's milk (WHO 1996; 2000). WHO (2000) lists the following dietary factors as major contributors to fluoride intake:

- Use of trona, $Na_3H(CO_3)_2.2H_2O$, in tenderising vegetables, e.g. in Tanzania where fluoride contaminated trona is known to have contributed significantly to dental fluorosis (Mabelya et al 1997 in WHO 2000).
- Consumption of high fluoride brick tea as a beverage, such as in Tibet (Cao et al. 2000) where people consume up to 14mg/day F from tea alone.
- Fly ash from fluoride-polluted coal in some regions in China contributes significantly to dietary fluoride exposure (Chen 1991).

Other sources of fluoride intake include infant formulas which can provide up to 1.0 mg F intake per day, dental products (including toothpastes) from which 0.4 mg F can be ingested in one mouthwash (NRC 1993). Dietary fluoride supplements are also common in the developed world.

Air is typically responsible for only a small fraction of total fluoride exposure, with the fluoride concentration in the air in non-industrial areas being in the range 0.05-1.90μg fluoride/m^3 (WHO 1996; 2000). However industrial production (and use) of phosphate fertilisers, burning of fluoride-containing coal and volcanic activity may elevate fluoride concentration in the air over an area leading to increased exposure via inhalation (WHO

1996; 2000). Indoor fluoride concentrations in some provinces in china range from 16-46 μg/ m^3 owing to indoor combustion of high fluoride coal for cooking and for drying and curing food (WHO 1996; 2000).

4

METHODS OF STUDY

4.1 SAMPLING PROCEDURES

Field sampling was conducted between May and August 2002. In this section, the sampling techniques, sample preservation procedures and sample container selection criteria employed are described.

Information from the Zimbabwe National Water Authority (ZINWA), which drills most boreholes in rural Zimbabwe, was used to locate the water sources. However, since some boreholes are privately sunk and since non-borehole water sources are also in use in Gokwe, the local communities themselves were very instrumental in locating the water sources. Indications were that water sources, particularly boreholes served large population catchments, implying that in total they are relatively few. A total of 242 water samples were collected from 214 water sources, possibly including all operational boreholes in the study area.

4.1.1 Sample Preparation

Samples from sealed boreholes serviced by pumps were collected by pumping water into the sample bottles, ensuring that the volume of water resting in the pipes was first expelled to minimise contamination from pipe fixtures. In the case of open wells, the water samples were collected manually with a plastic bailer which was thoroughly rinsed between water sources. All samples that were to be shipped to Curtin University, Western Australia for laboratory analysis by High Performance Ion Chromatography (HPIC) were filtered through Whatman no. 1 filter papers. Whatman no.1 filter papers were used because they are affordable, general-purpose filter papers sufficient for removal of any sediment suspended in samples. It is important to remove the suspension materials because they might undergo chemical changes before sample analysis, resulting in misleading analytical results. Solid particles can also potentially clog the HPIC separator columns. Blank analyses showed that the filter papers did not contain any fluoride or major ions that would contaminate samples.

Filtration was not required for samples measured for fluoride in the field with the fluoride ion selective electrode (FISE) because FISE measurements are not affected by sample colour or turbidity (see Advantages of ISE, p.59). However, a few samples that were particularly extremely murky were first filtered through Whatman no.1 filter papers before measurement to avoid soiling the FISE instrumentation.

4.1.2 Sample Holding Times and Preservation

All fluoride ISE determinations were undertaken the same day the water samples were collected and it was unnecessary to preserve them in any way. However samples for anion and cation analyses to be shipped to Curtin University, Western Australia, were frozen to increase the holding time. On shipping they were specially packed and arrived at Curtin in a semi-frozen state and were immediately refrigerated. Before analysis, the samples were first homogenised by shaking each fully thawed sample in its sealed container vigorously for at least 2 minutes. According to Harsham (1995), such homogenisation is necessary to combat any changes that may occur to solid residue, if any, on freezing and thawing.

4.1.3 Sample Containers

According to Harsham (1995), such factors as resistance to breakage, size, weight, interference with constituents, cost and availability should be taken into account when choosing sample containers. Water samples in this study were held only in clean fluoride free polyethylene bottles. Glass is generally not an ideal medium for holding samples for fluoride analysis (*Method 9214: Potentiometric determination of fluoride* 1996) because glass contains some fluorine. In addition, plastic is generally cheaper than glass and allows less metal adsorption. Table 4.1 compares glass and plastic containers:

Property	*Borosilicate glass*	*Conventional polythylene*
Interference with sample	Inert to all constituents	Good for most contituents
Weight	Heavy	Light
Resistance to breakage	Very fragile	Durable
Cleaning	Easy to clean	Some difficulty removing adsorbed components
Sterilisable	Yes	In some instances
Space	Takes up considerable space	Substantial space savings during extended field studies

Table 4.1: Comparison of glass and plastic as sample containers

Container preparation and washing

This study mainly utilised new sampling containers. Samples of the different plastic containers were filled with deionised water and left to stand for five days. The water was then analysed using High Performance Ion Chromatography (HPIC) to check for any contaminants that may have leached from the plastic. The results indicated that the containers did not release any contaminants to the water in quantities that could be detected (~1ppb).

In this study where pre-used containers were used, they were washed following the recommendations of Harsham (1995) given below:

(i) Wash the containers and caps with a non-phosphate detergent

(ii) Rinse with tap water, then distilled water [In this study, the containers were rinsed two times with distilled water then once with deionised water (>18 Ohm)]

(iii) Invert and drain dry

(iv) Visually inspect for any contamination prior to usage

(v) In this study all containers that were found wanting in step iv above were simply discarded.

One additional step was taken in this study: samples of cleaned containers were filled with deoinised water and left to stand for two days before analysing the water with HPIC (in the laboratory) or FISE (in the field). No detectable levels of any analyte of interest were recorded, thus demonstrating that the washing procedure was satisfactory.

Field blanks were tested once a day to check the accuracy and possible drift in FISE measurements.

4.2 ANALYTICAL METHODS

This study employed two main analytical techniques for determination of fluoride dissolved in water. The methods are the fluoride ion selective method (FISE) and the high performance ion chromatography (HPIC). FISE had the advantage of being utilised in the field, whilst the HPIC analysis was performed in the EIGG Laboratory, Curtin University.

4.2.1 Ion Selective Methods- Overview

Ion selective electrode (ISE) methods use electrodes or 'sensors' to determine the concentrations of various ions in aqueous solutions in a wide variety of applications. The most widely used ion selective electrode is the pH electrode, which contains a thin glass membrane that responds to the H^+ concentration in a solution and ISEs for other ions must have an equivalent membrane that is sensitive to the ion of interest and not to any interfering ions (*The University of Adelaide,* n.d.).

There are two main types of membrane material:

(i) Solid crystal matrix: single crystal or polycrystalline compressed pellet (F^-, Ce^{3+}, K^+ and Al^{3+})

(ii) Plastic or rubber film impregnated with a complex organic molecule which acts as an ion carrier.

The fluoride electrode was invented by Dr. Martin Frant in the early 1960s at Orion Research Inc. and laboratories have extensively used it since then (*Fluoride measurement*

2001). In this study, the Thermo Orion Model 290A with Thermo Orion Model 94-09 Half Cell Fluoride Electrode was used. The system reference electrode was the Thermo Orion 90-01 Single Junction Reference Electrode. The membrane was mono-crystalline lanthanum fluoride, doped with a small amount of europium to lower the bulk resistivity (50 000 ohms-100 000 ohms compared to several mega ohms for glass electrodes) of the crystal (Rundle 2000).

4.2.2 The Fluoride (and other) ISE

The special membrane allows only the passage of fluoride ions and when immersed in a solution, fluoride ions diffuse through the membrane until an equilibrium is reached between the internal and external concentrations (Rundle 2000). Because of the need for equilibrium conditions, there is very little current flow and so this potential difference can only be measured relative to a separate reference electrode which is also in contact with the solution, but is unaffected by it (Rundle 2000).

The potential difference developed across the membrane is directly proportional to the logarithm of the ionic concentration (more correctly, the activity) in the external solution. This relationship is given by the Nernst equation as follows:

$E = E' + (2.303RT/nF) \times \log(A)$

Where E = the cell potential in mV.

E' = a constant similar to, but not equivalent to E° for a redox couple

(except for a small liquid-liquid junction E°is a constant and is independent of sample composition)

2.303 = the conversion factor from natural to base 10 logarithm.

R = the gas constant (8.314 joules/degree/mole)

T = absolute temperature

N = the charge on the ion (with sign)

F = The Faraday Constant (96 500 coulombs).

Log (A) = the logarithm of the activity of the measured ion.

The factor 2.303RT/nF is known as the slope of the electrode (from the straight line of E versus log (A) which is the basis of the ISE calibration graphs) (Rundle 2000). At constant temperature, this should be constant depending on the valency of the ion being measured. Under normal circumstances, however, the slope varies between 50 and 60 mV for mono-valent ions (25-30 mV for divalent ions) because of variations in temperature, deviations from ideal behaviour and variable ionic conduction across the ion-selective membrane. This means that when measuring samples, a potential difference of about 55 mV can be expected for every 10-fold change in concentration, i.e. equivalent to 1 pH unit (1/log 10) in the case of a pH electrode (Rundle 2000).

In practice, when measuring concentration with modern ISEs it is not necessary to construct a calibration graph and interpolate the results for known samples because this is done automatically by the meter and the unknown concentration is calculated and displayed immediately (Rundle 2000).

Advantages of ISE

ISE methods of F^- analysis have the following strengths vis-a-vis other methods (Rundle 2000):

- ISE are relatively inexpensive and simple to use.
- ISE work in a wide concentration range.
- Most recent models are robust and durable and thus ideal for use in either the field or laboratory.
- Under the most favourable conditions in relatively dilute solutions with no interfering ions, ISEs can be used very rapidly and easily.
- In applications where interfering ions, pH levels or high concentrations are a problem, then many manufacturers can supply a library of specialised experimental methods and special reagents to overcome many of these difficulties, e.g. TISAB.
- With careful use, frequent calibration and an awareness of the limitations, they can achieve accuracy and precision levels of ± 2-3% for some elements and thus compare favourably with analytical techniques which require far more complex and expensive instrumentation.
- ISEs are unaffected by sample colour or turbidity.
- ISEs can be used in aqueous solutions over a wide temperature range. Crystal membranes can operate in the range 0°C to 80°C plastic membranes from 0°C to 50°C.

Limitations of ISE

In spite of their numerous applications and strengths, ISE measurements have a number of problems (Rundle 2000):

Ionic interference and selectivity coefficients

Most ISEs are to some extent sensitive to other ions (e.g. Al^{3+}, OH^- and Fe^{3+} in F^- measurements), although in many cases such interferences are insignificant and can be ignored. However, where there is a high concentration of the interfering ion or, in extreme cases where the electrode is more sensitive to the interfering than the primary ion, ion interference is of great concern

The selectivity coefficient refers to the ability of an ion selective electrode to distinguish between different ions in the same solution and depends on temperature, concentration of both ions and total ionic strength of the solution (Rundle 2000). If A is the primary ion and B the interfering ion, a selectivity coefficient of 0.1 would mean that the electrode is 10 times more sensitive to A than B; if it is 1, the electrode is equally sensitive to both.

The effect of ionic strength

The *ionic strength* (I) is a measure of the total effect of all the ions in a solution; it is the sum of the molar concentration multiplied by the square of the valency of all the ions, given by:

$$I = 0.5 \times \text{Sum} (ci \times Zi^2)$$

Where c is the concentration of ion I in moles and, Z is the valency

The effective concentration measured at the electrode head is known as the *activity* of the ion; it generally represents the number of ions taking part in a chemical reaction measured in concentration units. The ratio of the activity/ concentration is known as the *activity coefficient*, a variable factor that depends on the valency and ionic radius of the measured ion and the ionic strength. The activity coefficient is always smaller than one and becomes smaller as the ionic strength increases; thus the difference between the measured activity and the actual concentration becomes higher at higher concentrations. This causes two problems for ISE measurements (Rundle 2000):

- When constructing a calibration graph using concentration units, the line curves away from linearity as the concentration increases (it remains straight up to the highest concentrations if activity units are used). Thus it is necessary to measure many more calibration points to define the curve more precisely and allow accurate interpolation of sample of results.
- It is most likely that the sample solutions will contain other ions in addition to one being analysed and the ionic strength of the samples may be significantly higher than that of the standards. Thus there will be an incompatibility between the calibration line and the measured samples leading to errors in the interpolated results.

It is possible to calculate the activity coefficient for the primary ion in a simple pure solution where the composition and relative concentration of all the ions is known. Thus the measured activity can be converted into concentration results for simple solutions but in most practical applications, this is not possible or very difficult and time consuming.

In dilute solutions, the concentration of ions in equilibrium at the membrane surface is directly related to the total number of ions in the solution and it is not necessary to convert activity to concentration units.

Reducing the effect of ionic interference and ionic strength

In this study, both ionic interference and ionic strength have been eliminated using Total Ionic Strength Adjustment Buffer (TISAB). TISAB generally consists of 1M NaCl to adjust the ionic strength, acetic acid /acetate buffer to control pH and a metal de-complexing agent. Al^{3+} and OH^- and Fe^{3+} are the major interfering ions in F^- measurements. Al^{3+} binds (complexes) strongly with F^- in water causing readings that are much lower than actual (*Fluoride measurement* 2001). The hydroxide ion reacts with the lanthanum fluoride that constitutes the membrane of the electrode to form lanthanum hydroxide. This causes the release of extra F^- ions resulting in unstable readings higher than actual (Rundle 2000; *Fluoride measurement* 2001). The buffer decomplexes Al^{3+} bound F^- and acidifies the sample to keep the pH in the range 4 to 8 and hence ensures a low OH^- concentration. Excessive of Fe^{3+} concentration may, however, complex part of the fluoride in spite of the TISAB which is supposed to combat this. This problem may be overcome by using "standard addition" methods rather than "direct potentiometry" (Zellmer 1999).

TISAB, which does not contain the analyte or any likely interferent, when added in sufficient quantity to completely swamp the ionic effects of the host solutions, brings a uniform ionic strength to all samples and standards (*Method 9214: Potentiometric determination of fluoride* 1996; McCaffrey 1998; Rundle 2000).

Other methods that can be used to counter ionic interferences are as follows:

- Dilute the samples to a level where the ionic strength effect is insignificant, making sure that the detected ion is still within the linear range of the electrode.
- For samples with complex but unknown matrix, make up the standard in a similar solution which does not contain the detected ion, or any which would interfere with the measurement.
- Use standard addition method (or sample addition) where the voltage is measured before and after a measured small volume of standard (or sample) is added to a larger measured volume of sample (or standard) and the ionic strength not altered significantly.

Potential drift

When a series of standards are repeatedly measured, the electrode slope (difference between voltages in different solutions) remains the same but the actual value in mV generally drifts downwards. Constantly removing and replacing an ISE in different solutions will produce hysteresis effects, the extent of which depends on the relative concentrations of the new and old solutions. Thus if the same solution is re-measured after measuring a different one, it cannot be expected to give exactly the same voltage the second time. Reference electrodes have stable voltages over short periods of time but tend to suffer from slow drift in liquid junction potential when immersed for long periods.

To minimise drift, the indicator electrode is constantly immersed in a 1000 ppm solution (with the reference electrode removed) between each measurement. This will achieve the specified drift of 1mV per day (8 hours).

However for most ISE applications, including the current F^- study, potential drift is insignificant compared to the overall reproducibility and accuracy requirements (Rundle 2000).

Evaluation of the Effectiveness of Two TISAB formulations in Combating Ion Interferences

In the determination of fluoride by the fluoride ion selective method (FISE), polyvalent cations such as Fe^{3+} and Al^{3+} are known to form soluble complexes with fluoride resulting in less fluoride being detected by the electrode. Adding a total ionic strength adjustment buffer (TISAB) can eliminate or minimise this interference. There are a number of different TISAB formulations available and they may have different capacities in combating ionic interference. The effectiveness of two different TISAB formulations, a commercial one and one made in the laboratory, has been compared.

Materials and method

Fluoride content in samples was determined using the method of bracketing standards (standards that narrowly bracket the expected sample concentration) with the use of a Thermo Orion Model 94-09 Half Cell Fluoride Electrode and a Thermo Orion Model 290A meter. The system used the Thermo Orion 90-01 Single Junction Reference Electrode. The samples used in the experiment were tap water dosed with various concentrations of iron and aluminium, and 1 ppm fluoride standard similarly dosed. Fluoride standard solutions were prepared by diluting commercial standard F^- solution of 1000 F^- mg/L concentration (Aldrich®, Milwawkee, USA) with deionised water (>18ohm). The samples and standards were separately treated with TISAB III and "EDTA TISAB", ensuring that the system was accordingly calibrated for measurement with each TISAB using a two-point calibration (1 ppm and 10 ppm fluoride). Each of the samples was also analysed in the absence of TISAB.

The compositions of the TISAB formulations used in the experiment are characterised as follows:

TISAB III (commercially available)

Description: Orion ionplus TISAB II concentrate with CDTA

Ingredients: Deionised water

Ammonium chloride (NH_4Cl)

Ammonium Acetate (CH_3COONH_4)

CDTA ($C_{14}H_{22}NO_8.H_2O$)

Cresorel Red

CDTA TISAB (made in the laboratory)

References: Adriano & Doner 1982;

Preparation Procedure

- Accurately weigh 58g of sodium chloride into a clean container
- Accurately weigh 4g of CDTA into a clean container
- Place about 400mL of >18 ohm deionised (white) water in a 1L beaker
- Add57mL of glacial acetic acid
- Carefully add the weighed sodium chloride
- Carefully add the weighed CDTA
- Place the beaker into a cold water bath for cooling
- Calibrate the pH electrode using the 4.01 and 7.00 pH buffer solutions

- Immerse the electrode into the solution and slowly add6N NaOH solution until the pH is 5.2
- Cool the solution to room temperature
- Carefully transfer the solution to a 1L volumetric flask, dilute to the mark with deionised water

Results and discussion

Table 4.2 summarises the results obtained from the experiment:

Analyte	**Interference**	**Concentration (ppm)**					
		TISAB III		CDTA TISAB		Without CDTA	
		Mean value	*% RSD*	*Mean value*	*% RSD*	*Mean value*	*% RSD*
Tape water (~0.8ppm F)	10 ppm Al^{3+}	0.53	0.95	0.58	3.91	0.0017	6.51
Tape water (~0.8ppm F)	50 ppm Fe	0.72	1.56	0.67	2.49	0.0022	5.71
1 ppm F standard	5 ppm Al^{3+}	0.87	1.70	0.98	1.11	0.0064	2.32
1 ppm F standard	10 ppm Al^{3+}	0.74	0.58	0.97	1.16	0.028	0.028
1 ppm F standard	20 ppm Al^{3+}	0.58	0.75	0.79	1.65	0.006	6.93
1ppm F standard	30 ppm Al^{3+}	0.41	2.01	0.57	0	0.0028	2.93
1ppm F standard	50 ppm Al^{3+}	0.33	0	0.44	0.98	0.028	1.56
1ppm F standard	50 ppm Fe	1.08	4.03	1.0	0	0.0033	2.49

Table 4.2: The effect of Fe and Al ions on the fluoride concentration measured by FISE.

A comparison of the concentrations of fluoride measured without the addition of TISAB to samples with those measured with TISAB added confirms that TISAB frees more of the fluoride for measurement. The effect of TISAB is to complex the polyvalent cations thereby minimising their effects on the F^- ion (*Method 9214: Potentiometric determination of fluoride* 1996).

Al^{3+} in both tap water and the 1ppm fluoride standard interferes with the measurements and the effect increases as the concentration of Al^{3+} increases. From the results given in Table 4.2, it is apparent that in both tap water (~0.8ppm F) and the 1 ppm fluoride standard, CDTA TISAB is superior to TISAB III in combating Al^{3+} interference.

With respect to the interference of Fe, it appears that TISAB III and CDTA TISAB buffers are equally effective with both combating even at 50 ppm Fe.

Conclusion

CDTA TISAB compares favourably with the commercially available TISAB III in eliminating ionic interferences in FISE measurements.

4.2.3 The FISE Protocol Used in This Study

In the light of the evaluation of the effectiveness of TISAB (see foregoing experiment) and the work of others regarding F^- determination by FISE (e.g. Adriano and Doner 1982; *Method 9214: Potentiometric determination of fluoride* 1996), the following protocol was employed in the analysis of water samples in this study.

Apparatus

1. Thermo Orion Model 94-09 Half Cell Fluoride Electrode and a Thermo Orion Model 290A meter, with Thermo Orion 90-01 Single Junction Reference Electrode and filling solution. The system technical specifications are as follows:

   Optimum pH range: pH 4- pH 8

   Temperature range: 5°C to 80°C

   Optimum temperature: 25°C

   Recommended TISAB: CDTA TISAB (see section..)

   Electrode slope at 25°C: 54±5mV/decade

   Detection limit: 0.02 mg/L

Total measuring range: 0.02-1900 mg/L

Time for stable reading: 2-3 minutes

2. CDTA TISAB
3. Magnetic stirrer and bars
4. 1000ppm fluoride standard (Aldrich, Milwankee, USA)
5. Digital pipette
6. Deionised water

Procedure

A total of 242 water samples collected following the sampling protocol previously described were analysed for fluoride by the FISE method within 24 hours of collection at a field base station. The following analytical procedure was followed for all samples batches analysed:

1. The reference electrode was filled with the appropriate filling.

2. The FISE was calibrated using standards that narrowly bracketed the expected sample concentration
    - 20.0mL of the lower concentration standard and 20mL of CDTA TISAB were added to a clean 50mL polyethylene beaker.
    - The solution was stirred slowly on a magnetic stirrer.

- The electrode tips were immersed at least 2cm into the solution and the meter calibrated to the standard concentration
- The electrodes were rinsed and the procedure repated with the higher concentration standard.

3. Water samples were analysed as follows:
    - 20.0mL of sample and 20.0mL of TISAB were added to a clean 50mL polyethylene beaker and the solution stirred slowly on a magnetic stirrer.
    - The electrode tips were immersed at least 2cm into the solution and the concentration recorded as soon as the reading was stable, and within 3 minutes of immersion.
    - The electrodes were rinsed prior to analysis of the next sample.

The following precautions were taken:

- The FISE was calibrated at the beginning of each session and after every 10 samples or after every hour of continuous measurement, and
- The concentration was recorded no more than 3 minutes after immersing the electrode tips, with care being taken not to immerse the electrodes in solutions containing TISAB for extended periods.
- The filling solution was changed wherever the FISE had not been used for more than a week and care was taken to ensure that there was sufficient filling solution in the in the reference electrode.
- Field blank solutions were analysed once a day.

Other measurements

At the well-head, pH, temperature, conductivity and total dissolved solids (TDS) for each sample were measured using portable meters on an aliquot separate from the one taken for FISE analysis.

4.2.4 High Performance Ion Chromatography (HPIC)

Of the 242 water samples collected in the field and analysed by FISE, a total of 159 duplicate samples were analysed for fluoride and common anions and cations by the HPIC instrumentation (Dionex® 4500i) at Curtin University.

For anion analysis, a Dionex® AS12A-AG12 column set was employed with Na_2CO_3 (2.7mM) and $NaHCO_3$ (0.3mM) eluent at a flow rate of 1.5mL min^{-1}. For cation analysis, a CS12A-CG12 column set was used with 0.22mM H_2S0_4 eluent at a flow rate of 1mL min^{-1}.

4.3 COMPUTER-BASED METHODS

4.3.1 Initial Data Capture

A database of results was constructed using MS ACCESS software. UTM coordinates and locality names of data collection points and element-by-element analytical results for each sample were stored in the database. The geographical coordinates were obtained in the field with the aid of a GARMIN 12 GPS receiver fed with appropriate projection information.

4.3.2 GIS Manipulation

Relevant 1:50 000 topographic maps and available geological maps (Ait-Kaci Ahmed *in prep.* and Leyshon 1969) were digitised into ArcView® GIS, capturing THEMES such geology, rivers, schools, contours, roads and other physical features. The resulting SHAPEFILES were converted into ArcInfo™ COVERAGES by taking advantage of the interoperability between the two GIS packages. ArcInfo™ was the preferred platform for correcting spatial errors in the digitised data and once corrected, the ArcInfo™ COVERAGES were converted back to the ArcView® GIS SHAPEFILES ready for manipulation and display. The resulting GIS database, in ArcView® GIS, was connected to the MS ACCESS database and the location and water quality parameters georeferenced. Using several tools in ArcView® GIS, such as the QUERY BUILDER, and utilities available in the SPATIAL ANALYST extension of ArcView® GIS, the data were available for GIS manipulation allowing for correlating fluoride concentrations to geology, creating fluorosis risk maps and creating water level contours and other maps contained in this thesis.

4.3.3 Other Computer Programs

ArcView® GIS has been coupled with ROCKWORKS to provide insight into lithostratigraphic aspects of the study area that may be important in the distribution of fluoride contamination in water supplies. Lithostratigraphic logs were constructed on the ROCKWORKS platform raw data sourced from the ZINWA and other sources.

MAPINFO was also used in spatial analysis just for comparative purposes, but its output has not been included in the present work because its output appeared inferior compared to that of ArcView® GIS.

5

RESULTS OF THE STUDY

In this chapter the results of the analyses of water samples collected from the study area are presented. Brief comments focused on the statistical analysis of, and discernible patterns from the results are included, but the extensive interpretation of the results is reserved till Chapter 6.

5.1 Overview of Results

A total of 242 water samples were collected in the field from 214 water sources, including 28 duplicate samples and 18 samples from just outside the study area. Of the 242 water samples, 102 were collected from pumped boreholes, 34 from artesian boreholes, 41 from deep (5m or deeper) open wells, 28 from shallow (<5m deep) wells, 8 from streams 19 from shallow riverbed diggings, 3 from springs and 6 from dams. Two further samples of filtrate from a village salt making plant were obtained and will be considered separately. In addition, results of previous Zimbabwe National Water Authority (ZINWA) sampling programmes of 12 boreholes from the study area are given in Appendix 2.

The parameters measured from water samples in this study may be divided into three categories:

1. Field parameters: temperature, pH, electrical conductivity and TDS.
2. Major dissolved ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-}, Cl^{-}, SO_4^{2-}, and NO_3^{2-}

3. The fluoride ion, F^-

The physical parameters were determined on all samples. All the 242 water samples collected were analysed in the field for fluoride using the fluoride selective electrode (FISE) method. One hundred and thirty seven of the samples were analysed for fluoride in the laboratory.

5.2 Fluoride Concentrations

Comparison of FISE and HPIC Results of Fluoride Determination

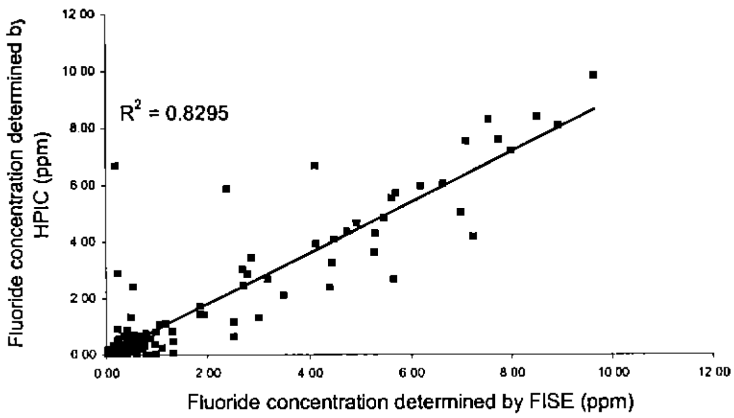


Figure 5.1 Correlation of the results of fluoride determination with FISE and HPIC

The fluoride concentrations for each sample obtained by the FISE and HPIC methods were paired and plotted against each other (Figure 5.1). As can be seen from the plot, the correlation was good (R^2 0.8295). However some individual samples show pronounced differences between results obtained by the two methods. McCaffrey (1998) explained a similar imperfect match for samples in his study as resulting from the water dip in the HPIC chromatograms. He suggested that the dip affected the fluoride peak baseline leading to inaccurate measurements for some samples. In this study, the baseline for all samples was manually optimized to counter the effect of the dip and to eliminate noise in the chromatograms, but the effect may not have been completely eliminated in some cases. The longer holding times for the HPIC samples compared to the FISE samples, and the freezing and thawing to which the former were subjected, may have allowed some slight changes in their chemical composition.

Breakdown of Fluoride Concentrations by Types of Water Sources

The fluoride FISE results will be used in this subsection to look into the results in more detail because the FISE measurements were performed on all samples, unlike the HPIC measurements. Moreover, as shown above, there is good agreement between the FISE and HPIC method and using either of them will not make a significant difference. Only the samples collected within the confines of the study area will be used and duplicates have been incorporated using the arithmetic mean. Thus 196 fluoride concentration results from 196 water sources are considered in this subsection.

Table 5.1 shows the number of samples from different water sources in different ranges of fluoride concentration.

Water Source Type	**Range of fluoride concentration (mg/L)**											
	>0 5		0 5-1 5		1 5-3.0		3.0-6 0		6 0-10.0		Total	
	No.	%	No.	%	No.	%	No.	%	No	%	No	%
Pumped Bores	29	37.2	22	28.2	8	10 3	11	14 1	8	10.3	78	100
Artesian Bores	0	0	0	0	2	12 5	9	56.3	5	31 3	16	100
Deep Wells	23	56.1	15	36.6	2	4.9	0	0	1	2.4	41	100
Shallow Wells	23	88.5	3	11.5	0	0	0	0	0	0	26	100
Streams	5	71.4	2	28.6	0	0	0	0	0	0	7	100
Riverbed Wells	13	68.4	6	31.6	0	0	0	0	0	0	19	100
Springs	1	33.3	1	33 6	1	33.3	0	0	0	0	3	100
Dams	5	83.3	1	16.7	0	0	0	0	0	0	6	100
TOTAL	99	50.5	50	25.5	13	6.6	20	10.2	14	7.1	196	100

Table 5.1: Fluoride concentration ranges for samples from different water sources.

Forty-seven (24.0%) of the 196 water sources yielded water with fluoride at concentrations above the WHO (1984; 1996; 2000) upper limit of 1.5 mg/L, and 50

(25.5%) water sources yielded water with the 'optimum' fluoride content in the range 0.5-1.5 mg/L. The remaining 99 (50.5%) water sources yielded fluoride-deficient water. The health implications of these ranges of fluoride concentration are given in Chapter 3 and are extensively discussed in Chapter 6.

Figure 5.2 shows the frequency percent of various ranges of fluoride concentration as determined in samples from all the water sources in the study area. The Figure shows that the largest number of water sources yielded water within the two lowest concentration ranges (<0.5 mg/L F and 0.5-1.5 mg/L F). In Figure 5.3, the breakdown of these fluoride concentrations by type of water source is given.

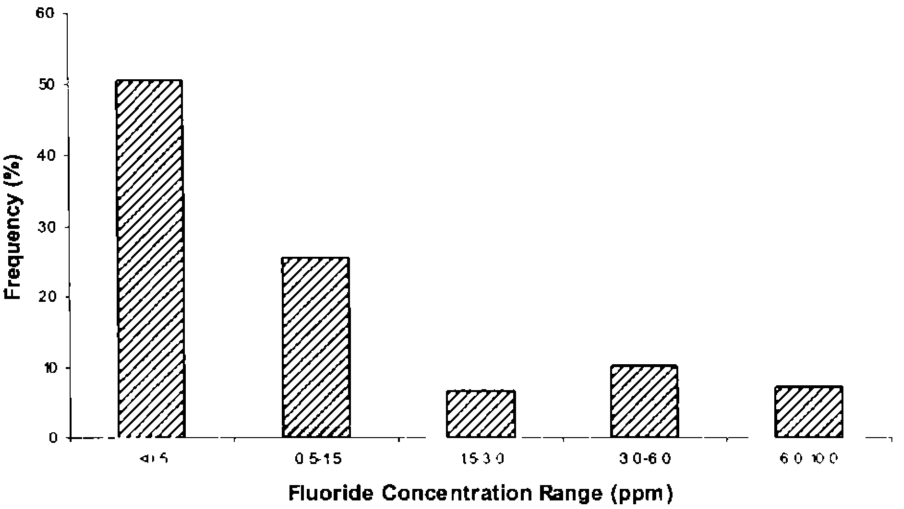


Figure 5.2: Frequency percent of the various fluoride concentration ranges recorded from water samples from all water sources

It can be seen from Figure 5.3 that shallower water sources (shallow wells, deep open wells, streams and dams) generally yielded low fluoride waters High fluoride waters (fluoride concentration above the WHO 1.5 mg/L guideline) dominantly came from pumped boreholes and artesian boreholes. Of the 14 samples falling within the 6.0-10.0 mg/L fluoride range, 8 were collected from pumped boreholes, 5 from artesian boreholes and the remaining one sample came from a deep open well.

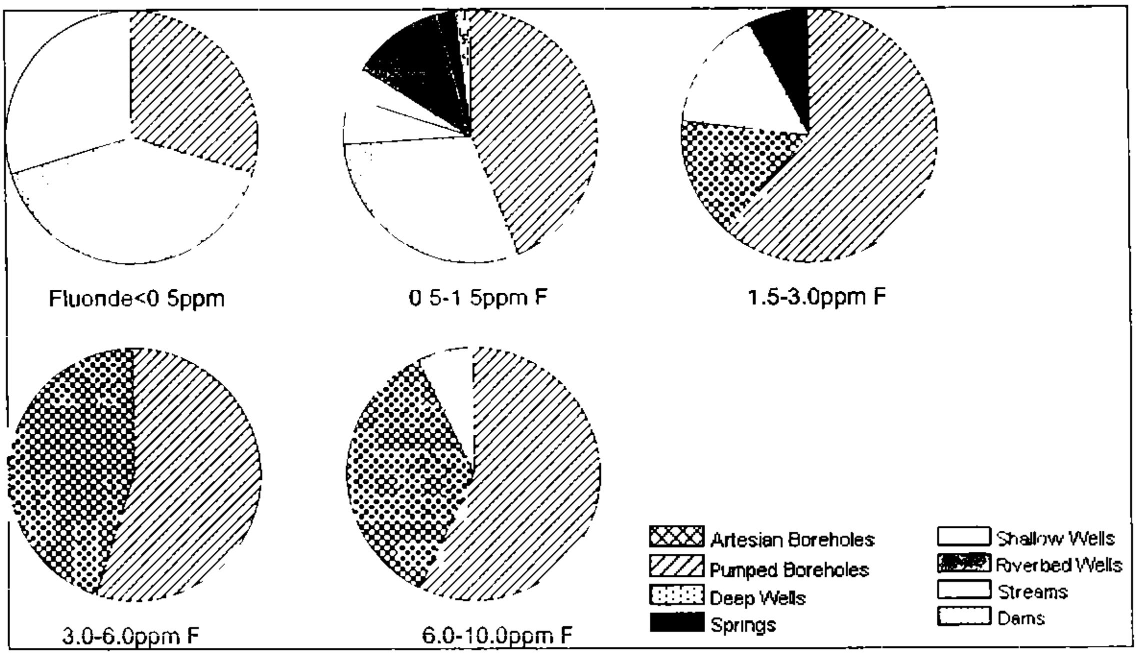


Figure 5.3: The contribution of each water source type to each fluoride concentration range as determined in respective samples.

A total of 20 samples had fluoride levels in the range 3-6 mg/L, all originating from artesian boreholes (9) and pumped boreholes (11). In the lowest two ranges, artesian boreholes are not represented and in the 1.5-3.0 mg/L range, artesian boreholes contributed only 2 (15%) of the 13 samples. The bulk (62%) emanated from pumped boreholes, with the rest shared between deep wells (15%) and springs (8%). A total of 149 samples had fluoride levels less than 1.5 mg/L; 51 of these (34.2%) were collected from pumped boreholes, 38 (25.5%) from deep wells, 26 (17.4%) from shallow wells and 19 (12.8%) from riverbed wells/ diggings. The remaining 10.1% came from streams, springs and dams. The fluoride concentrations of water collected from pumped boreholes appear to have the widest spread across all the fluoride concentration ranges. This is shown more clearly in Figure 5.4.

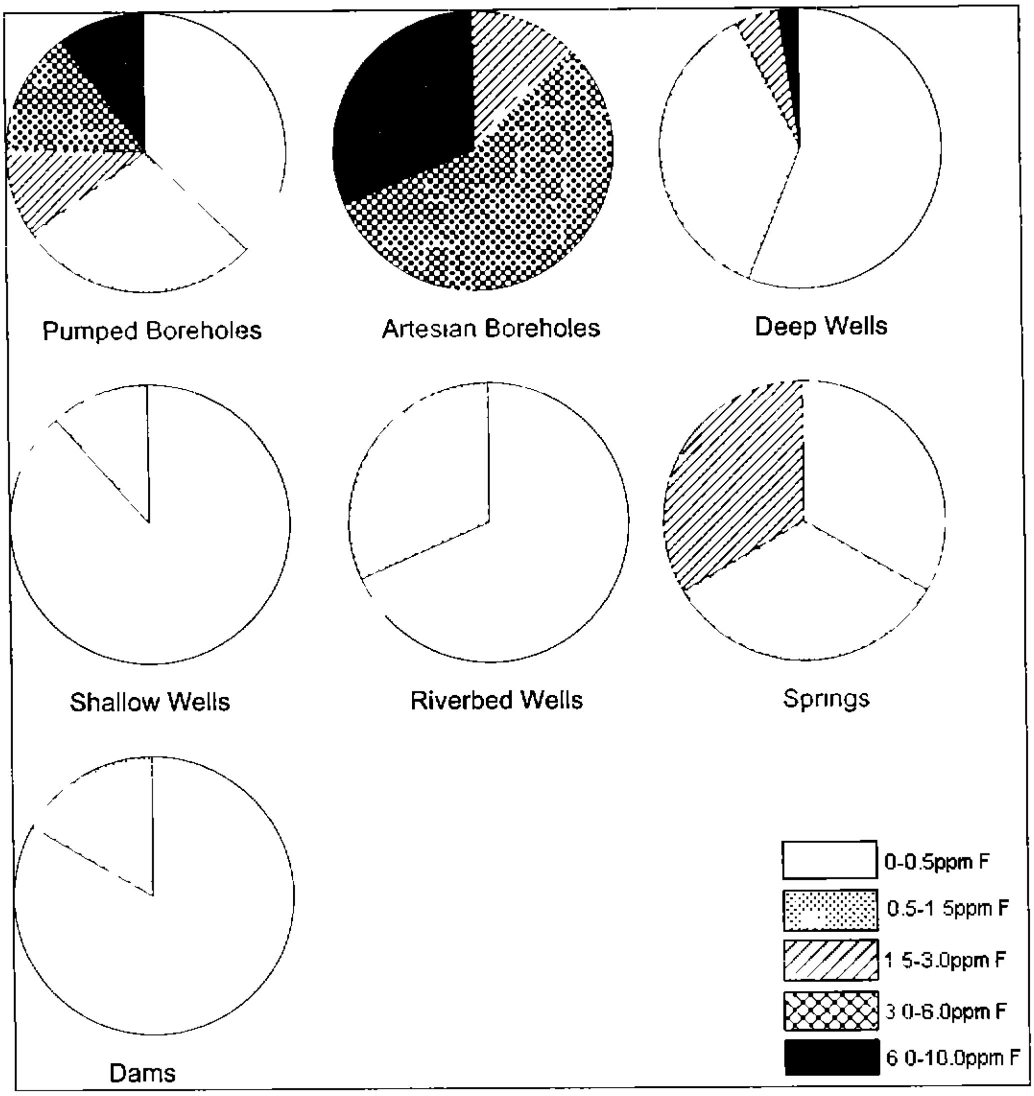


Figure 5.4: The ranges of fluoride concentration determined for samples from each type of water source.

5.3 Major Ion Concentrations and TDS

The concentrations of chloride, nitrate and sulphate, sodium, potassium, magnesium and calcium were determined for 129 samples using HPIC. Table 5.2 and Figure 5.5

summarise the analytical results of major ions from the 129 samples, in relationship to WHO (1993) guidelines for drinking water quality. The full list of results is shown in Appendix 1.

Parameter	Range (mg/L)	Average (mg/L)	WHO limit (mg/L)	N>limit	Remarks
Cl^-	0.056-8748.263	144.35	250	13	Cl>250mg/L can give objectionable test and may increase metal corrosion rates resulting in increased metal concentrations in the supply (WHO 1993)
NO_3^-	0-1542.293	26.66	50	7	By conversion to nitrite, may cause methaemoglobinaemia, unconfirmed link to cancer (WHO 1993)
SO_4^{2-}	0-1199.603	106.11	500	7	May cause detectable test and at >500mg/L, health officials must be notified (WHO 1993)
Na^+	0-3468.153	177.11	200	31	Na> 200mg/L may cause unacceptable taste (WHO 1993). DEP (2001) suggests that Na>160mg/L aggravates sodium sensitive hypertension and diseases that cause difficulty in regulating body fluid volume.
K^+	0-98.037	7.61	-	-	-
Mg	0-319.916	21.71	-	-	-
Ca^{2+}	0-17767.590	161.63			-
TDS	0.778-14750	823.04	1000	20	Health-TDS relationship not known, but TDS>1000mg/L causes objectionable test in drinking water (WHO 1993).

Table 5.2: The levels of major ions and TDS in the drinking water supply of the study area, with respect to WHO (1993) guidelines.

Table 5.2 and Figure 5.5 suggest that the major ions of some concern in the water supply of the study area are sodium, sulphate and nitrate. The water sources with relatively elevated sodium levels (Na>200 mg/L) were pumped boreholes (15), artesian boreholes (11), deep wells (3) a riverbed well and a stream. Sources that yielded water with sulphate at concentrations greater than 500 mg/L were 2 riverbed wells, 1 stream, 2 deep wells, 1 artesian borehole and 1 pumped borehole. Excessive chloride (Cl>250 mg/L) was contained in water from pumped boreholes (6), artesian boreholes (5), a deep well and a riverbed well. Nitrate-rich waters (NO_3^->50 mg/L) were obtained from 4 deep wells, 2 shallow wells and an artesian borehole. Eight pumped boreholes, 8 artesian boreholes, 3 deep wells and 1 riverbed well yielded water with relatively elevated levels of total dissolved solids (TDS>1000 mg/L).

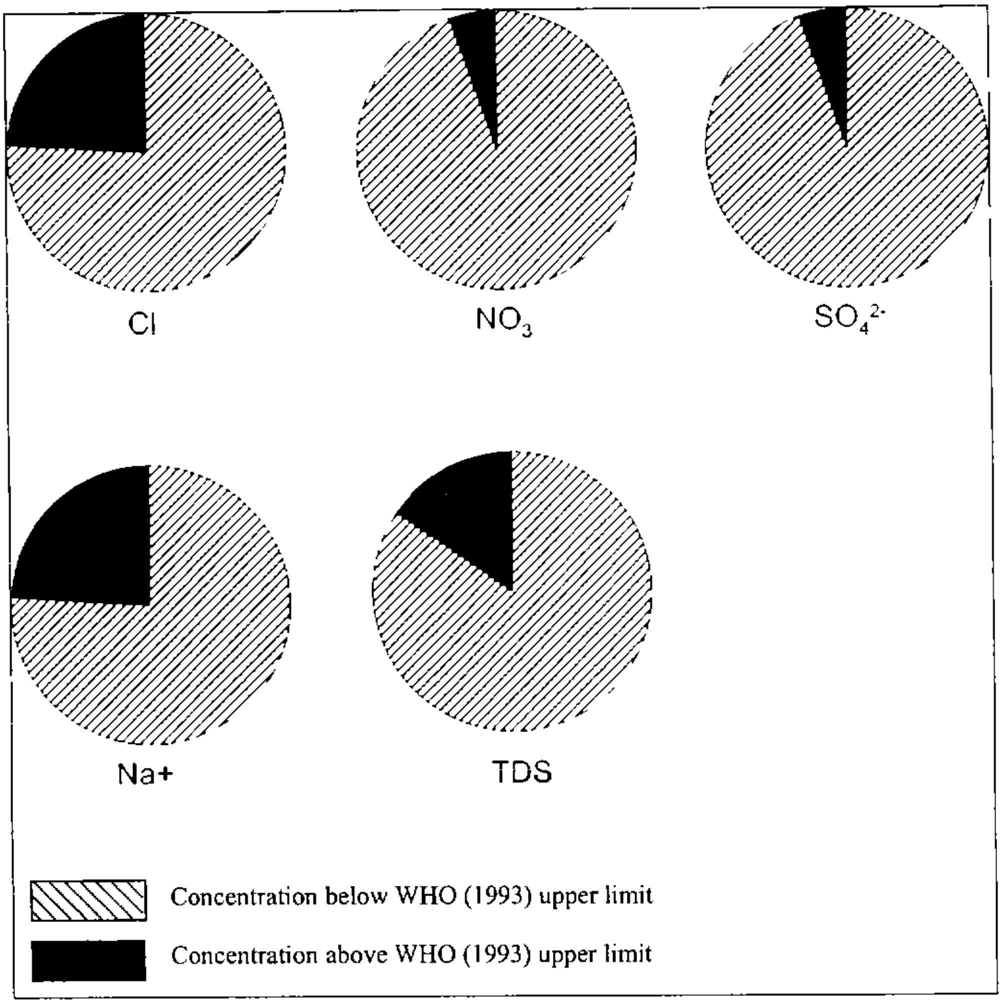


Figure 5.5: Proportion of water sources issuing water with chemical parameters above and below WHO (1993) upper limit. The WHO limits are given in Table 5.2.

It would appear that high levels of sodium, chloride and TDS are generally associated with deeper water sources (pumped and artesian boreholes, and to a lesser extent deep wells). High nitrate levels appear to be largely associated with shallower water sources. In the case of sulphate, it appears there is no bias towards any particular type of water source.

5.4 Bari Salt Pan Samples

At Bari Salt Pan (centred on borehole WB2 at 666906E, 8058789N) two salts are locally recovered from water filtered through soils placed on filtration beds. The salts are then recovered by the rapid evaporation of water from the filtrate by boiling. One of the salts ('soda') is used as a meat and vegetable tenderizer and the other ('salt') is used as table salt. Samples of both salt filtrates were analysed and the following results were obtained:

Sample	F (FISE)	F (HPIC)	Cl	NO_3	SO_4	Na	K	Mg	Ca
w057 'Soda'	160.0	122.71	26529.60	638.89	21.65	1947.52	2448.93	222.84	627.50
w058 'Salt'	9.56	9.54	16760.98	580.67	1110.58	378237.80	12376.56	154.215	26.53

Table 5.3: Analytical results of Bari salt filtrates. The elemental concentrations are in mg/L.

It appears from the results that sample w058 was largely NaCl and w057, which effervesced profusely on addition of dilute HCl, contained carbonate and could have been trona, $Na_3H(CO_3)_2.2H_2O$. While the 'soda' filtrate contained much more fluoride, the 'salt' filtrate was also fluoride- rich. However, a sample of salt produced by the village plant from an aliquot of the high-fluoride filtrate measured only 1.5 ppm F on the HPIC. Does the boiling drive off (volatile) fluoride? Samples of prepared 'soda' were not available.

6

DISCUSSION

6.1 GEOLOGY AND FLUORIDE DISTRIBUTION

In Chapter 5, the results of fluoride analysis were presented and grouped according to fluoride concentration ranges and type of water sources from which the samples were obtained. In this section, ArcView® GIS has been employed to investigate and display any relationships between the fluoride concentrations in drinking water and the spatial distribution of lithological units associated with the water sources. To establish the variation of fluoride concentrations with down-hole geology, ROCKWORKS has been used to construct and stratigraphic logs and stratigraphic cross-sections from raw borehole log data.

The geological maps of Ait-Kaci Ahmed (*in prep.*) and Leyshon (1969) have been used as base maps for the central and eastern parts of the study area respectively. The central part of the study area, which is covered by a more detailed geological map and which contains the 'type-stratigraphy' of the area, is illustrative of the relationships between rock units and fluoride concentration in water supplies. A rich archive of borehole log data of both coal exploration and water supply boreholes has greatly complemented the understanding of the relationships in the central part of the study area. In contrast, the geological map of the eastern part of the study area (Leyshon 1969) has limited lithological detail with respect to Karoo rocks, and borehole log data could be obtained for only a few boreholes in the area. Because of this, the discussion of apparent

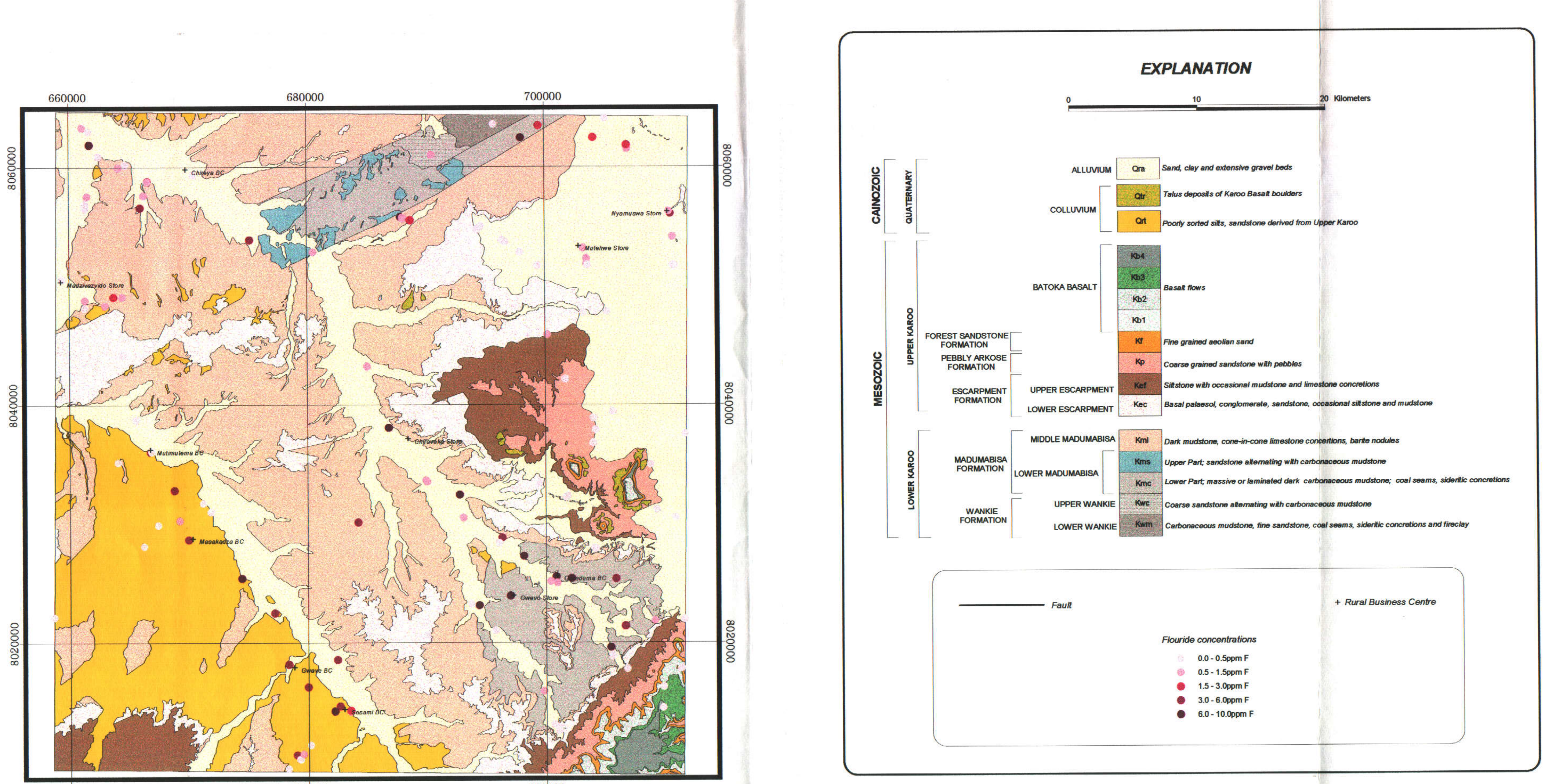


Figure 6.1: The concentrations of fluoride in water with respect to the location of water sources on the geological map. The geology was mapped by Ait-Kaci Ahmed (in prep.) This map was compiled and digitised by Mamuse (this thesis). The grid is UTM (Zone 35).

associations between geology and fluoride distribution in the eastern part of the study area will be limited to those places where stratigraphy similar to that of the central part is expected.

6.1.1 Fluoride Distribution in the Central Part of the Study Area

Figure 6.1 shows the location of all water sources in the central part of the study area with respect to surface geology. Table 6.1 summarises the *apparent* associations between surface geology (rock type at the collar of each water source) and the fluoride content of the water from the source, as suggested in Figure 6.1. This subsection discusses the validity of the associations and ultimately, by means of selected key borehole logs, a suite of materials that may be the potent source of fluoride contamination in the area is isolated.

Lithology	**Number of water sources in each fluoride concentration range**					
	0-0.5 mg/L F	0.5-1.5 mg/L F	1.5-3.0 mg/L F	3.0-6.0 mg/L F	6.0-10.0 mg/L F	Total
Qra	41	19	3	7	6	77
Qrt	12	3	1	7	1	23
Qtr	0	0	0	0	0	0
Kb	2	0	0	0	0	2
Kf	1	0	0	0	0	1
Kp	4	0	0	0	0	4
Kef	2	0	0	0	0	2
Kec	4	0	0	0	0	4
Kml	2	6	1	1	1	11
Kms	0	0	0	0	0	0
Kmc	0	1	1	2	5	9
Kwc	0	1	0	0	0	1
Kwm	1	0	0	0	0	1
Kwf	0	0	0	0	0	0
Total	69	30	6	17	13	135

Table 6.1: The apparent correlation between surface geology and fluoride concentration in drinking water from water sources. The abbreviations under 'lithology' are explained in Figure 6.1.

For convenience, some of the more important attributes of key boreholes frequently cited in this section are listed in Table 6.2. The complete set of attributes of all the sampled water sources is given in Appendix 1.

Borehole ref. No.	**Borehole official name**	**Easting**	**Northing**	**Sample ID**	**F conc. (mg/L)**
B2	6G	670278	8028664	w044	5 730
B3	6 GO N-091	702407	8025377	W017	7 555
B5	6 GO S 174	669080	8032829	w050	5 310
B6	6 GO-N 090	693034	8032444	w093	7 260
B7	6 GO S 095	683820	8014309	w107	2.870
B8	Coko	679593	8010167	No sample	-
B9	6-GO-S-184	659689	8059575	w103	0.329
B10	-	658752	8049792	w104	2 690
B11	WB6	697274	8023933	w005	8.940
B12	WB1	666881	8058769	w059	4.76
B13	WB7	684524	8030102	w097	4 12
B14	WB8	706902	8021381	w018	5.49
B15	WB9	698421	8027272	w029	6.65
B16	WB2	0666902	8058798	w056	4.48

Table 6.2: Attributes of selected boreholes

6.1.1.1 Superficial Deposits and Fluoride Distribution

Table 6.1 shows that 100 of the 135 water sources in the central part of the study area were sunk on superficial deposits, namely Quaternary Alluvium and Quaternary Colluvium. The Table also suggests that the water sources sitting on the superficial deposits constitute about two-thirds (25 out of 36) of the water sources bearing water with fluoride contents higher than the WHO guideline value of 1.5 mg/L F. However, all the 25 high fluoride water sources sitting on superficial deposits are pumped boreholes (10), artesian boreholes (12) and deep wells (3). These high fluoride boreholes are likely to be tapping water beyond the superficial deposits and it could be the deeper geological units that accounted for the elevated levels of fluoride. For example, according to the lithologic log of borehole B6 (Figure 6.2), the borehole sits on Quaternary Alluvium but it also cuts through 70.2 m mudstone, 162.4m of coaly shale and penetrates 24.7m into sandstone. Clearly in such a setting the water chemistry, including fluoride content, may not be attributed to the surface geology.

The remaining 75 water sources on the superficial deposits yielded relatively low-fluoride water. Sixtyfive of these low fluoride water sources are shallow sources (shallow wells, shallow riverbed pits, dams and streams) fully hosted in, and therefore tapping water from, the superficial deposits. The other 10 sources are boreholes, such as B7 at Sesami Mission and B9 at Madzivazvido Clinic, which penetrate beyond the superficial deposits but extend into other units that may also be fluoride poor. This argument will be further developed in subsection 6.1.1.3. It is evident that water that emanates from the sources entirely hosted in superficial deposits has low fluoride levels. Accordingly, the superficial material cannot be considered a source of fluoride contamination in the study area.

6.1.1.2 The Upper Karoo and Fluoride Distribution

A total of 13 water sources sampled in this study sit directly on different lithologic units of the Upper Karoo and all of them yielded water containing less than 0.5 mg/ L fluoride (Table 6.1). These water sources include 2 boreholes, 4 deep wells, 4 shallow wells, 1 stream and 2 riverbed wells. From these observations, it can be concluded that there is no evidence to link any of the Upper Karoo lithologic units to fluoride contamination in the area. It must be mentioned that two of the wells were entirely hosted in Karoo Basalt. Thus, the speculation of Magalela (1997) linking fluoride contamination of the drinking water in the study area to Karoo Basalts (Kb) must be discarded and, regarding the basalts, the observation of INTERCONSULT^{AS} (1985, p. 39) may be correct: "The quality of the groundwater in this unit (Karoo Basalt) is always good, with TDS normally <1 000 mg/L. The water does not pose any fluoride hazard, although it may pose a mild encrustation hazard in places. The water is suitable for human consumption".

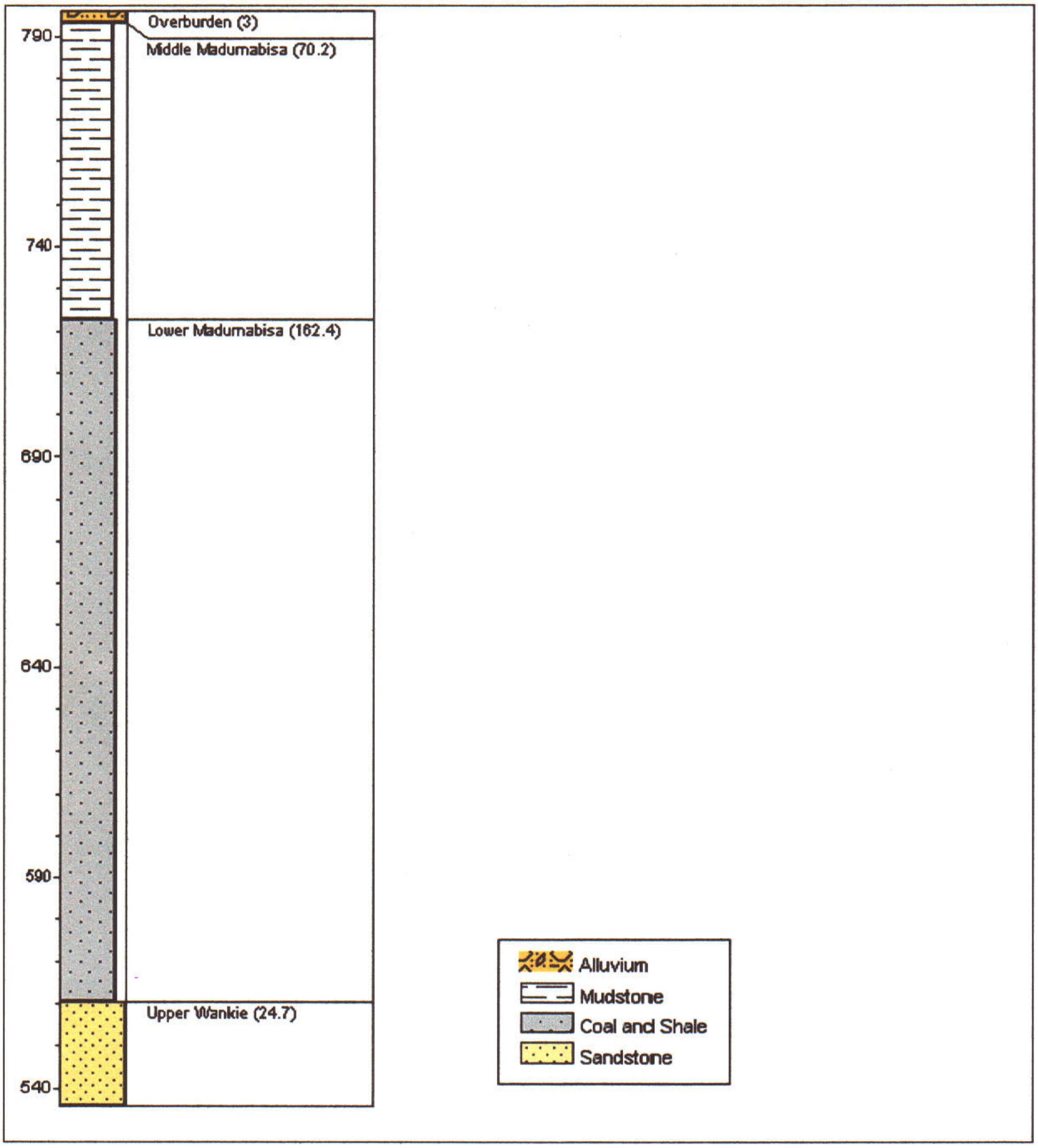


Figure 6.2: Lithostratigraphic log for Denda Clinic artesian borehole (B6). Elevations are in metres above MSL and stratigraphic thicknesses (in parentheses) are in metres. The log data were obtained from ZINWA.

6.1.1.3 The Lower Karoo and Fluoride Levels

A total of 22 water sources included in this study sat directly on a Lower Karoo lithological unit. From Table 6.1, it can be seen that four units of the Lower Karoo Supergroup, namely Middle Madumabisa Member (Kml), Lower Madumabisa Member (Kmc), Upper Wankie Sandstone (Kwc) and Middle Wankie Member (Kwm) hosted a water source collar. Table 6.2 gives more details about the water sources on the Lower Karoo Units.

Lithology	**Average F (mg/L)**	**Number of water sources**				
		Boreholes	Shallow sources	F<1.5 mg/L	F>1.5 mg/L	Total
Kml	1.3558	2	9	8	3	11
Kmc	5.4977	5	1	1	8	9
Kwc	0.505	1	0	1	0	1
Kwm	0.325	0	1	1	0	1

Table 6.3: Fluoride levels of water sources of the Lower Karoo Supergroup

From Table 6.3, the Lower Madumabisa Member (Kmc) readily shows a strong association with high fluoride levels. Eight of the 9 water sources sitting on the Kmc yielded water with fluoride levels greater than 1.5 mg/L, averaging 6.21mg/L. 3 of the 8samples were collected from artesian boreholes and 4 from pumped boreholes. The ninth sample was collected from a shallow well on a riverbed. This sample, strictly speaking, cannot be considered to have come from the Kmc but from a superficial sand deposit.

For the Middle Madumabisa Member (Kml), 3 (1 pumped borehole, 1 artesian borehole and 1 spring) of the 11 sources had water with fluoride levels greater than 1.5 mg/L, whereas the remaining 8 are shallow low-fluoride water sources. Two other low-fluoride water sources, a stream flowing on the Middle Wankie Member (Kwm) and a borehole on the Upper Wankie Sandstone (Kwc) were also sampled and their respective fluoride concentrations are shown on Table 6.3.

The shallow water sources sitting on Middle Madumabisa Member (Kml) are likely to be largely tapping water from within that unit only. On the other hand, the three high-fluoride water sources, particularly the two boreholes, are possibly tapping water from beyond the Middle Madumabisa Member. One of the boreholes, B13 (at Umbe Primary School) was initially drilled for coal exploration, and it yielded water containing 4.12 mg/L F (sample w097). During drilling in 1951, strong artesian flow of water forced the workers to abandon the borehole 'hastily before samples of the seam (of Middle Wankie coal) which was being approached could be taken' (*Report on prospecting operations in eastern Sebungwe* 1951, p. 17). This statement suggests that the borehole, though sitting on the Middle Madumabisa Member, penetrated the Middle Wankie (possibly the roof to the coal seam) before it was abandoned. The other borehole at Chomukuyu Primary School is not artesian and yielded water containing 7.12 mg/L F (sample w145). Log data (Global Literature Life Boreholes 1990) of a borehole close to, and sitting on the same geological position as, the Chomukuyu Borehole (A. Ait-Kaci Ahmed 2003, pers. comm., 20 January), will be considered. The log data indicate that the borehole traversed into the Middle Madumabisa Member and the Lower Madumabisa Member (total 116 m), Upper Wankie Sandstone (5 m) and shales of the Lower Wankie Member (29 m). In such a case, the source of fluoride contamination can be any combination of the geological materials involved. Figures 6.3 and 6.4 show that the shallower pumped borehole at Sesami Mission that terminates within the Middle Madumabisa Member is fluoride poor. In this study, all the water sources fully hosted within the Middle Madumabisa Member are fluoride-poor and those penetrating beyond the member are fluoride-rich. It can therefore be concluded that the Middle Madumabisa Member is not the source of fluoride contamination in the area and that the fluoride comes from units stratigraphically below the member.

It has been shown that the high-fluoride boreholes that sit on superficial deposits tap water beyond the deposits. These deposits generally sit on Lower Karoo topographic lows rather than on the Upper Karoo topographic highs. Figures 6.2, 6.3 and 6.8 show logs of boreholes that sit on superficial deposits but which penetrate the Madumabisa Mudstones (Kml and Kmc) and beyond. Most other high fluoride boreholes that sit on superficial deposits, such as Mudondo School Borehole (B14), Kahobo Clinic Borehole (sample w096) and Gwave Artesian Borehole (sample w012) may have a similar down-hole geological setting. The *Report on prospecting in eastern Sebungwe* (1951) indicates that borehole B14 penetrated the Middle Wankie Member and intersected a seam of 'dull shaly coal' with a thickness of 6 metres (see Appendix 5).

The Wankie Formation, which has a limited outcrop, only has two water sources directly associated with it, namely a stream flowing on the Middle Wankie Member and a borehole on the Upper Wankie Member. Both yielded water with fluoride less than 1.5 mg/L, but results from water sampled on a flowing stream are of doubtful significance.

However, the low fluoride content of water from the borehole may suggest that Upper Wankie Sandstone is not a source of fluoride contamination. Low fluoride (0.33 mg/L) was also detected in water (sample w103) from borehole B9 (Fig. 6.9), which is 90 m deep and fully hosted in alluvium-covered Upper Wankie Sandstone. Further significance of the results from B9 will be discussed later in this sub-section.

Up to this point it has been shown that the potent source or source (s) of fluoride lie stratigraphically below the Middle Madumabisa Member, possibly excluding the Upper Wankie Formation. In addition, a strong but not conclusive association between the Lower Madumabisa Member (Kmc) and high fluoride levels has been suggested. Three questions remain to be answered: (1) Which specific lithological units of the Lower Madumabisa Member, if any, are associated with the high levels of fluoride in drinking water in the area?; (2) Is any of the other units of the Wankie Formation (Middle Wankie Member and Lower Wankie Member, having excluded the Upper Wankie Member) a potent source of fluoride contamination?; and (3) What other factors, lithostratigraphical or otherwise, may also be at play in fluoride contamination of water supplies in the area? Answers to these questions will now be pursued by studying and interpreting lithostratigraphical data of selected key boreholes, a cross section of which is shown in Figure 6.9.

To begin with, two boreholes at Sesami Mission will be considered. They are situated 160 m apart and both sit on Quaternary Colluvium (Fig. 6.9). One is a pumped borehole, 35m deep, from which sampled water (sample w107) contained 0.66 mg/L F. The other

(B7) is an artesian borehole, 228m deep, from which sampled (sample w108) water contained 2.87 mg/L F. Figure 6.3 shows the lithologic log for the artesian borehole, with equivalent depth (35m) of the shallower pumped borehole indicated. The marked difference in fluoride content of water from the two neighbouring boreholes suggests that in terms of lithologic units intersected in the bores, differing aquifer units have been hyped. The pumped borehole terminates 13.7 m into a 169.5 m thick mudstone. B7, on the other hand, traverses the whole thickness of the mudstone and the next three underlying units. It is likely that this additional thickness, or part of it, accounts for the difference in fluoride levels. The stratigraphic log of B7 in Figure 6.3 shows limited detail. Therefore, a lithostratigraphical correlation with strata at borehole B8 (Figures 6.4 and 6.5) was performed to probe the missing detail. Borehole B8, located 6 km to the SE of the artesian borehole, was drilled for the purpose of coal exploration and was logged in great detail.

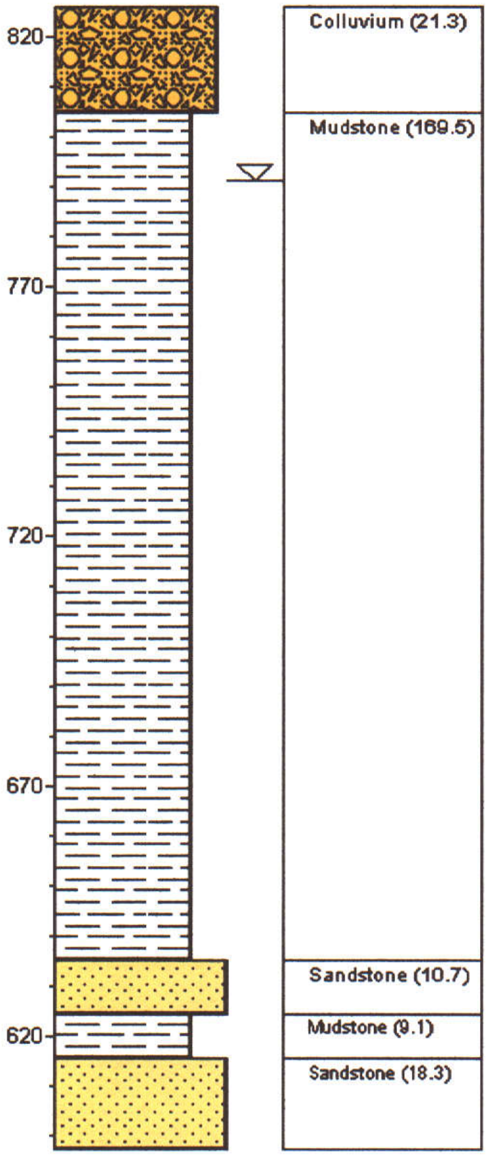


Figure 6.3: The litholostratigraphic log of borehole B7 at Sesami Mission. The level marker indicates the bottom of the nearby pumped borehole. Elevations are in metres above MSL and the stratigraphic thicknesses (in parentheses) are in metres. The log data were obtained from ZINWA.

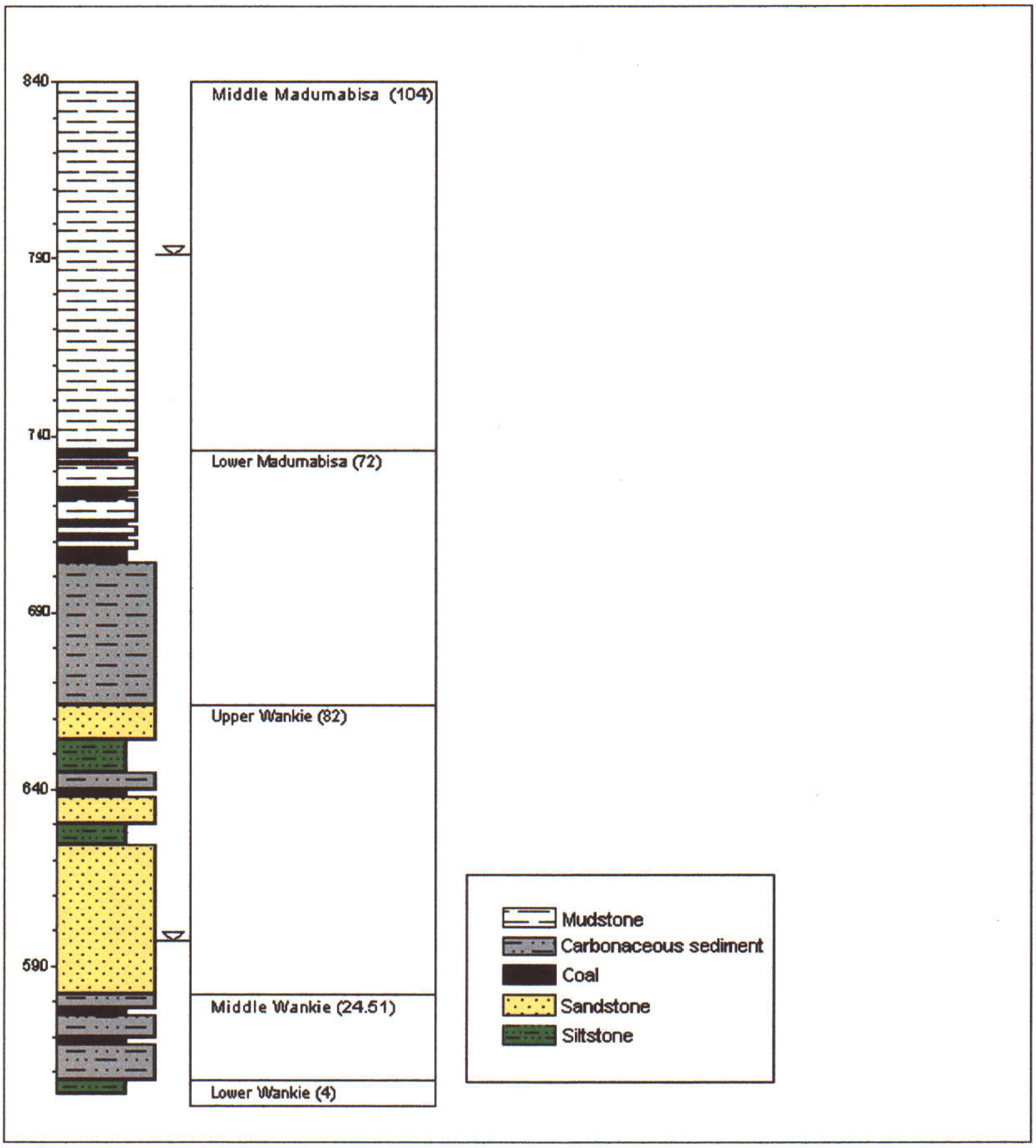


Figure 6.4: The lithostratigraphic log of borehole B8. The lower and upper triangle markers are the translated bases of the Sesami artesian and pumped boreholes. Elevations are in metres above MSL, and stratigraphic thicknesses (in parentheses) are in metres. The lithologic data were obtained from Lepper (1992).

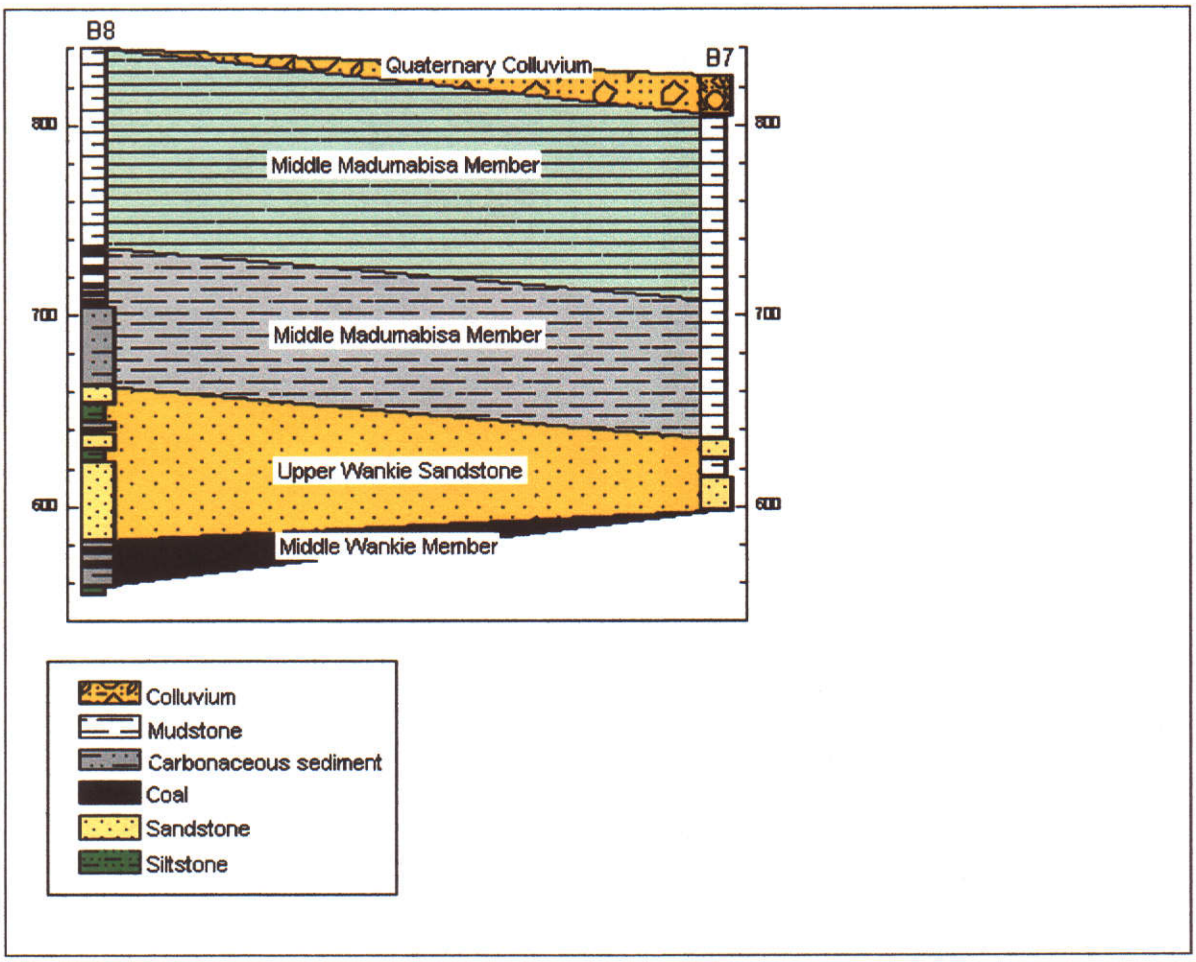


Figure 6.5: Lithostratigraphic correlation across B8 and B7 boreholes. Elevations are in metres above MSL.

It has been assumed that the two boreholes have essentially similar lithostratigraphy and this interpretation is shown graphically in Figure 6.5. From Figure 6.3 and Figure 6.4, it is clear that the more fluoriferous artesian borehole penetrates the following additional lithostratigraphic units not penetrated by the less fluoriferous pumped borehole:

Lower Madumabisa Member: coal, carbonaceous sediment

Upper Wankie Member: sandstone, siltstone, carbonaceous sediment, coal

It is likely that it is from all or some of the additional lithologic units that the artesian borehole acquires excess fluoride. However it must also be noted that there is a significant difference in calcium concentrations between B7 (4.04 mg/L Ca) and the pumped borehole (13.17 mg/L Ca). It has been mentioned in Chapter 3 that fluoride solubility is commonly negatively related to the concentration of calcium in natural waters.

Further useful observations may be made at Sesami. B7 is less than 20m short of penetrating another lithological assortment of the Wankie Formation (Fig. 6.4). The assortment consists of siltstones, coal and carbonaceous sediments which, from the foregoing, are eminent fluoride contamination candidates. It is therefore logical to consider boreholes that penetrate these additional lithologic units. (B8 cannot be used because no sample was collected from it as it has long been plugged) Borehole B11 is an artesian bore originally drilled for coal exploration. Water from the borehole (sample w005) contained 8.94 mg/L F. Figure 6.6 shows that the borehole is largely hosted within carbonaceous sediments, although it also passes through intervening sandstones of the Wankie Formation. The log of borehole B2, an artesian borehole at Masakadza is shown in Figure 6.8. The well yielded water (sample w044) containing 5.73 mg/L F. The borehole penetrates the Middle Wankie Member which, at this point, consists of a 'coal and shale' unit. Apart from penetrating an additional stratigraphical level with carbonaceous and coaly (Middle Wankie Member), B8 and B11 intersected greater thicknesses of carbonaceous and coaly material compared to B7. The carbonaceous and coaly material is therefore a very likely source of fluoride contamination.

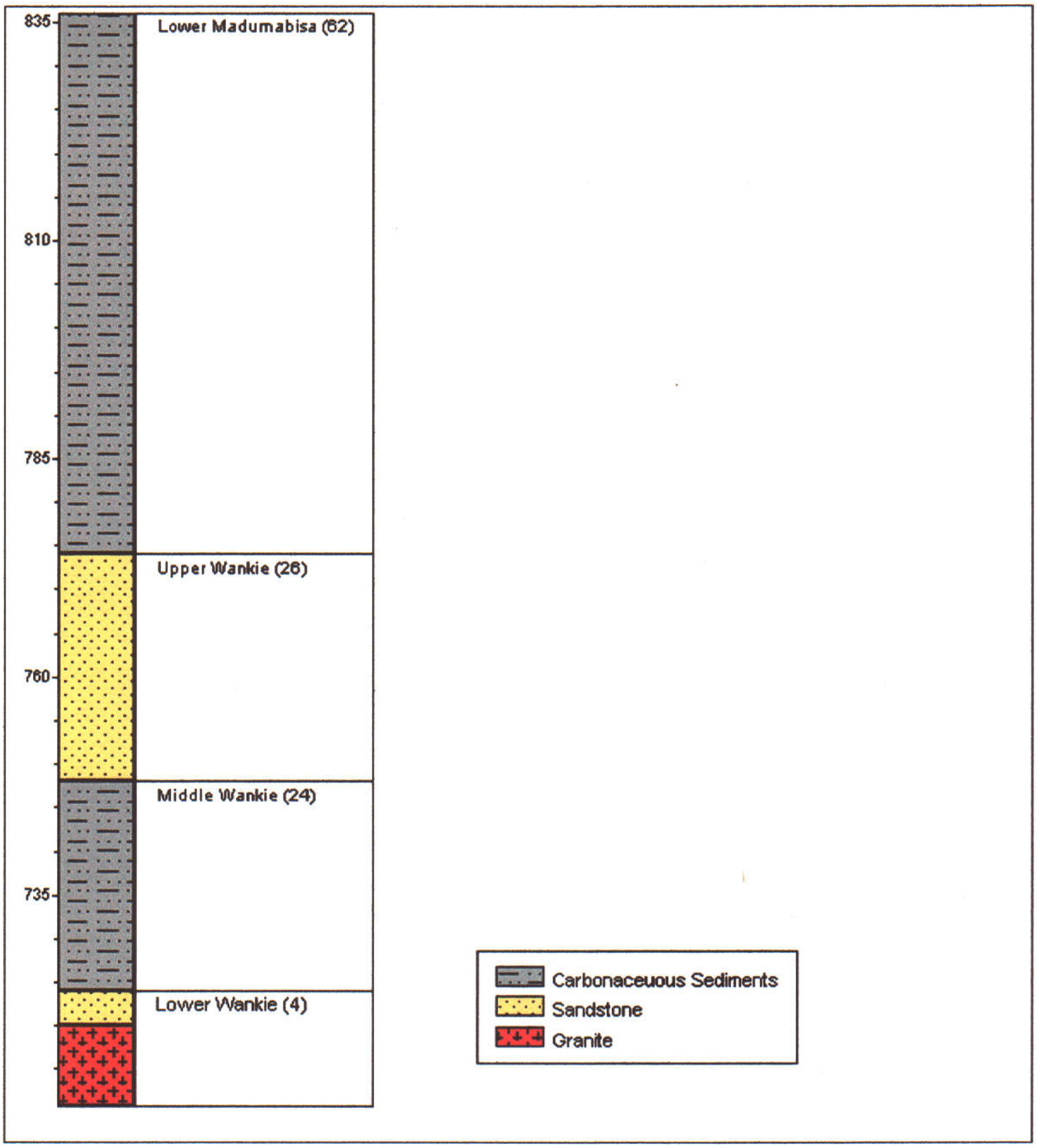


Figure 6.6: Lithostratigraphic log for borehole B11. Elevations are in metres above MSL, and stratigraphic thicknesses (in parentheses) are in metres. The log data were obtained from Lepper (1992).

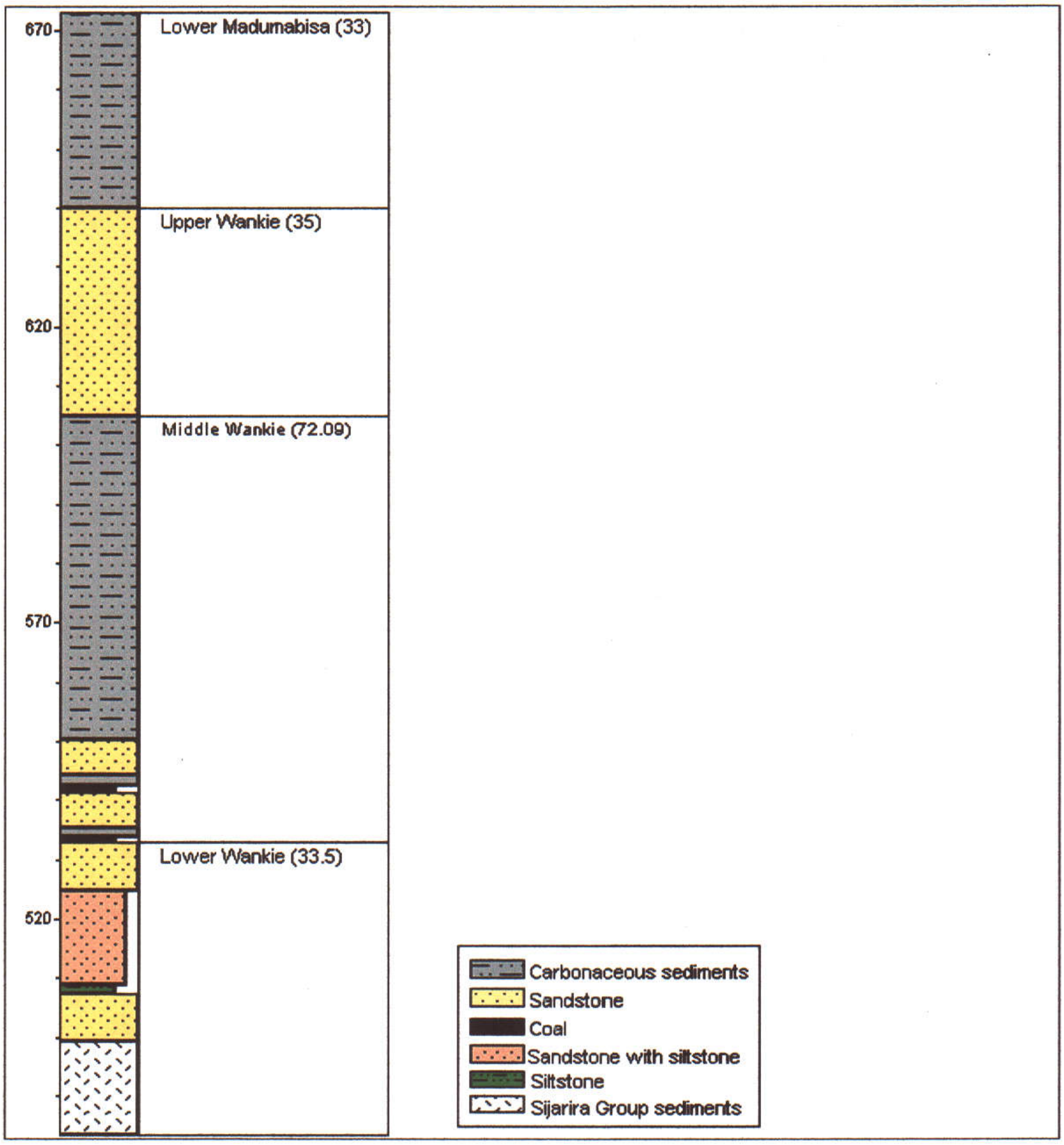


Figure 6.7: Lithostratigraphic log for borehole B12. Elevations are in metres above MSL, and the stratigraphic thicknesses (in parentheses) are in metres. The log data were obtained from Lepper (1992).

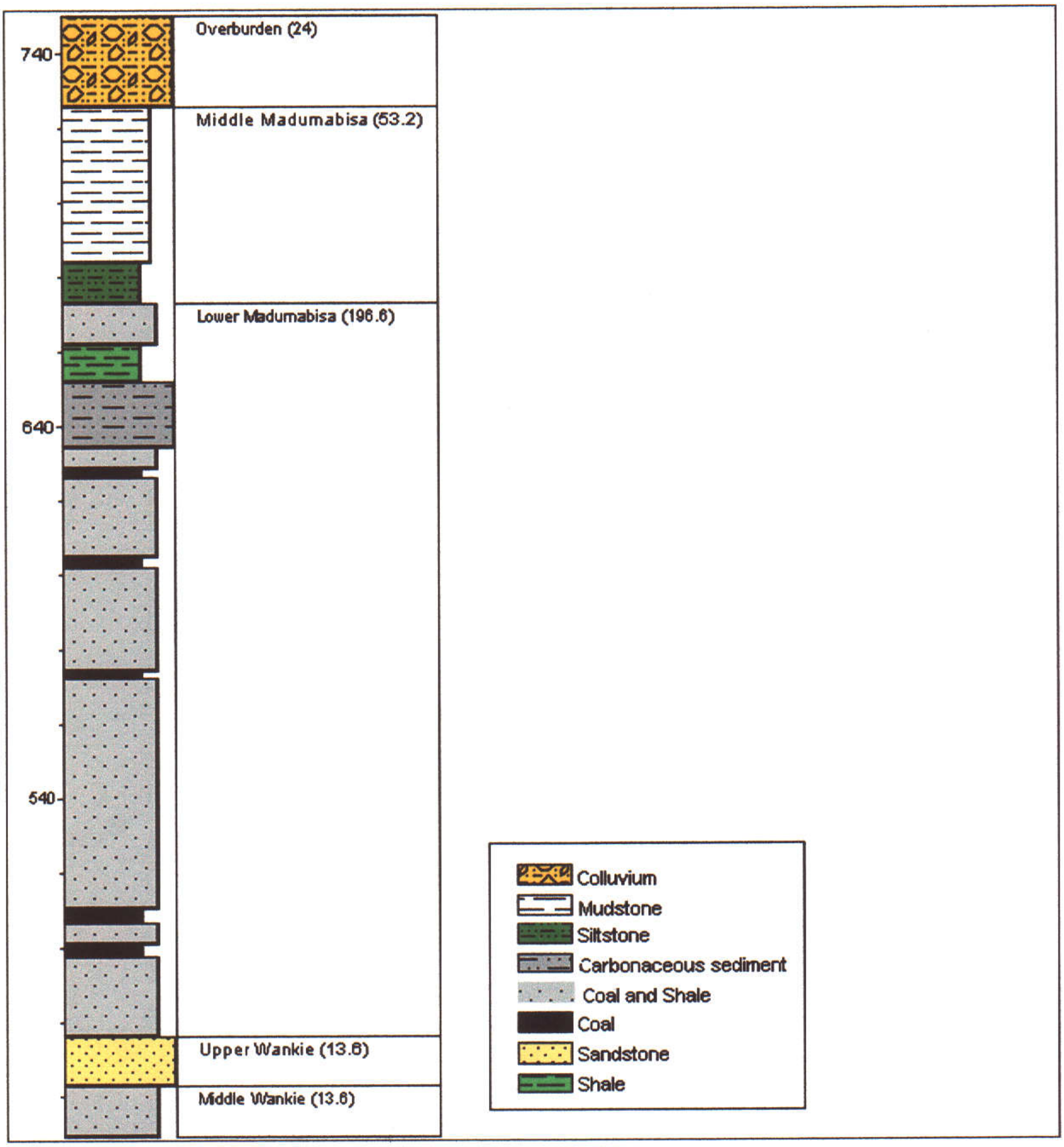


Figure 6.8: Lithostratigraphic log for borehole B2. Elevations are in metres above MSL ant the stratigraphic thicknesses (in parentheses) are in metres. The log data were obtained from Garande (1990).

A situation comparable to that at Sesami appears to exist at Madzivazvido where B9, a pumped borehole and B10, an artesian borehole lie 1.3 km apart (Fig. 6.9). The pumped borehole sits on Quaternary Alluvium (Figs. 6.1 and 6.10) and is fully hosted in 70 m of sand and 20 m of sandstone (Upper Wankie Sandstone). It has been assumed that the 70 m of sand consists of about 20 m of Quaternary Alluvium and 50 metres of *insitu*-weathered Upper Wankie Sandstone, although the original ZINWA log data (Appendix 4) do not show these distinctions. Water sampled from B9 (sample w103) contained 0.33 mg/L F whereas that from B10 (sample w104) contained a higher F concentration of 2.69 mg/L F. From Figure 6.9, it appears that in the likely situation that the artesian borehole (B10) is deeper than the pumped borehole (B9), B10 may have penetrated the Middle Wankie Member. If this is correct, then the Middle Wankie Member, encountered in B10 and not in B9, may be the source of fluoride contamination.

In comparison to, for example water from B8 and B11,water from B10 has a relatively low level of fluoride contamination. This can be explained by the absence of the Madumabisa Formation, expected to occur above the Wankie Formation, at B9 (and B10) (Fig 6.9). B10 is thus spared of additional fluoride contamination from the potentially fluoride-bearing carbonaceous material of the Lower Madumabisa Member, unlike B8 and B11.

The absence of the Madumabisa Formation at B9 and B10 can be attributed to the observation that in the study area, Lower Karoo rocks 'were subjected to gentle folding and trough faulting followed by a period of erosion so that a great amount of material has been removed' (Sutton 1979, p. 200). The erosional unconformity has been cited as the reason for the absence of Upper Madumabisa Member in the whole study area and the absence of the Middle Madumabisa Member in the Goredema area to the SE of the study area (see Fig. 6.10), and elsewhere at the foot of the Mafungabusi Plateau (Bond 1955; Bohmke & Duncan 1974; Sutton 1979; Ait-Kaci *in prep.*). An exposure of the Upper Wankie Sandstone on the Chota Uplift (Ait-Kaci Ahmed, *in prep.)* to the NE of B9 and B10 suggests a localised, but complete, removal of the Madumabisa Formation (see Fig. 6.9). According to Ait-Kaci Ahmed (*in prep.)* the Chota Uplift was generated by successive NE trending faults. It is therefore not improbable that at B9 and B10, which lie on the same fault zone as the exposure to the NE, the Madumabisa Formation was entirely eroded following fault-induced uplift. B9 and B10 sit within a valley of a major river and it may be this river or its palaeo-equivalent that removed the Middle Madumabisa Member. The uplift is evident on Figure 6.10, which shows relative up-arching of the Upper Wankie Sandstone Formation at B9 (and B10) compared to B5 and B12.

6.1.1.4 Geology and Fluoride Distribution in the Central Part of the Study Area: A Synopsis

The distribution and concentration of fluoride in drinking water in the central part of the study area is evidently related to the lateral and vertical distribution of geological materials. Virtually all the lithological units of the Upper Karoo Supergroup, including the Batoka Basalt may be discarded as the fluoride source. Rather, the fluoride contamination appears to emanate from carbonaceous and coaly lithologic units of the Lower Madumabisa Member and the Middle Wankie Member. The evidence in support of this conclusion has been discussed and is summarised and further developed with the aid of a cross-section though key boreholes (Fig. 6.9). The locations of the key boreholes are shown on Figure 6.10.

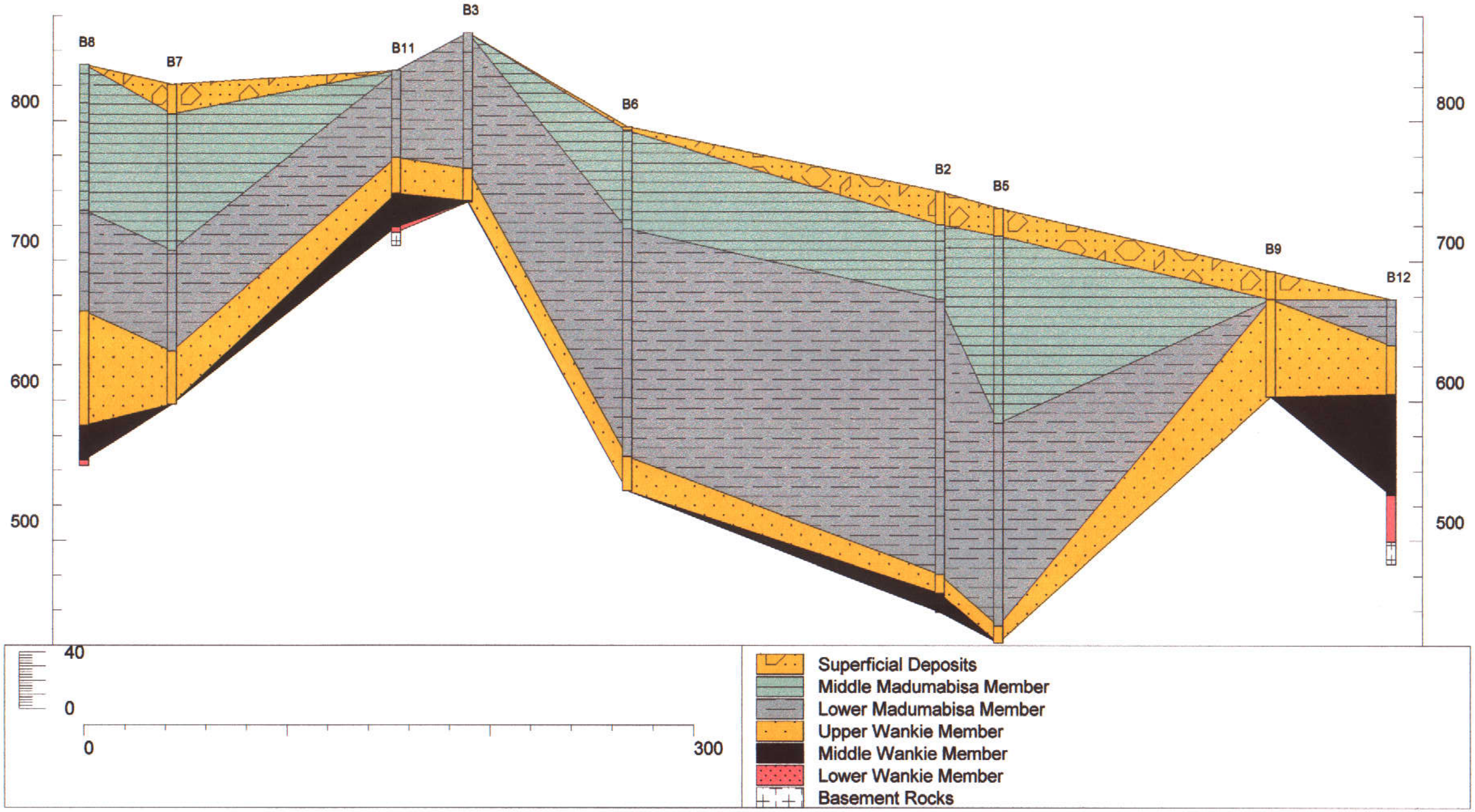


Figure 6.9: Cross-section through key boreholes. Raw log data were obtained from different sources cited elsewhere in this thesis. The cross-section and its inherent assumptions and interpretations are the full responsibility of Mamuse (this thesis). The elevations are in metres above MSL, and the horizontal scale is in UTM metres (eastings). Vertical exaggeration is 150X.

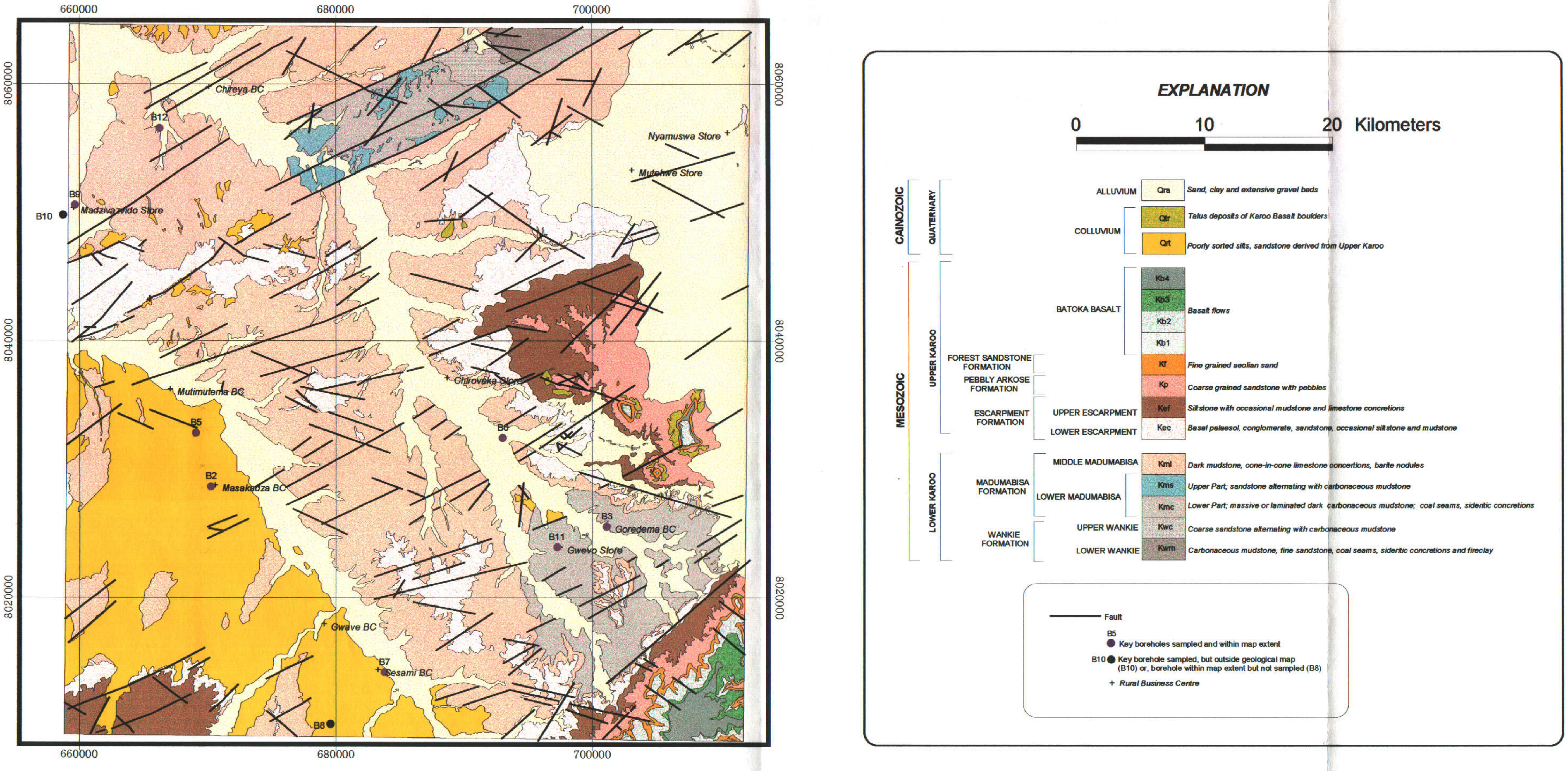


Figure 6.10: The location of key boreholes with respect to rock type and faults. The geology was mapped by Ait-Kaci Ahmed (in prep.) This map was compiled and digitised by Mamuse (this thesis). The grid is UTM (Zone 35).

The intensity of fluoride contamination in the water supplies of the study area is generally directly related to the proportion of the carbonaceous material that the well intersects. The 'carbonaceous material' in the area variously consists of carbonaceous mudstone, carbonaceous shale and sub-bituminous to high-volatile bituminous coal, with the coal occurring as seams or dispersed lenses within the mudstones and shales (Lepper 1992). In terms of hydrogeology, these fine-grained sequences generally serve as regional confining beds for the artesian system in the area (INTERCONSULT^{AS} 1985; Ait-Kaci Ahmed, *in prep.*). Such fine-grained sedimentary rocks, which usually act as aquicludes, can however provide storage for vast quantities of water, contributing significant drainage into wells, particularly where differential hydraulic heads are large enough (Davies & DeWiest 1966). [It has been reported that the coal in the study area had a high moisture content ranging from 8.05-9.4% by weight (*Report on prospecting in eastern Sebungwe* 1951)]. It is likely that the pervasive E- and NE-trending faults in the area, which chiefly affect the Lower Karoo (Ait-Kaci-Ahmed *in prep.*), greatly enhance the water-bearing capacity of the shales and mudstones. In laboratory experiments in the UK, the Chalk of Britain gave hydraulic conductivitiy values between 10^{-3} m/day and 10^{-2} m/day, translating into transmissivities of less than 5 m^2/day, but transmissivity measurements from wells in the Chalk gave values exceeding 1000 m^2/day (Price 1996). The huge difference was attributed to the presence of fissures, thought to contribute more than 99% of the transmissivity and almost the whole of specific yield, although contributing only 1% of the porosity of the fine-grained Chalk (Price 1996). These comments suggest that the water-bearing capacity of the fine-grained pervasively faulted carbonaceous material in the study area may be significant and must not be overlooked.

Thus the fluoride contamination of water in the area can be explained by the drainage of fluoride-rich water from the carbonaceous material to wells. The extent of this contamination depends on the volume and the fluoride concentration of the fluoride-rich water, both of which may depend on the proportion of the carbonaceous material intersected in the well. Figure 6.7 shows that borehole B12 passes through carbonaceous material of both the Lower Madumabisa Member and the Middle Wankie Member. However, the fluoride content of the water (sample w059) was 4.76 mg/L F, about half that of the water from B11. Based on the lithostratigraphic logs shown in figures 6.6 and 6.7, it has been calculated that B11 intersects carbonaceous material constituting 67 % of the aquifer thickness while in B12 carbonaceous material constitutes 49 % of the intersected aquifer thickness. Table 6.4 shows the fluoride contents of water from selected boreholes with respect to the percentage of carbonaceous material constituting the aquifer. From the Table, it appears that, the greater the proportion of aquifer units consisting of carbonaceous material, the higher the fluoride content of the water. However, some departures from this observation can be noted. B3, with carbonaceous material constituting 75.2 % of intersected aquifer thickness, yielded water with slightly lower fluoride than B11 with carbonaceous material making up 66.7 % of the intersected aquifer thickness. This can be explained by the fact that for B11 (Fig. 6.6), the proportional contribution of the water derived from the carbonaceous material to the total well yield may have been underestimated by the inclusion of the basement granite in the calculation. Though a substantial thickness of the granite is intersected in the bore, the water from the granite may not be volumetrically significant compared to the total well yield. This is because secondary permeability structures such as faults and joints, which almost entirely control the water-bearing capacity of granites, tend to close at depth due to the weight of overlying material (Davis & DeWiest 1966; Price 1996). The relatively low fluoride content recorded in water from B2 may be due to the elevated levels of calcium in the water (sample w044, 15.89 mg/L Ca). The concentration of fluoride at B12 is consistent with the proportion of carbonaceous material in the bore, but the relatively high concentration of calcium (sample w059, 12 mg/L Ca) may also be contributory factor to the relative suppression of fluoride content. The negative correlation between fluoride solubility and calcium is discussed in Chapter 3. Calcium concentrations of the water from the other boreholes are 0.11 mg/L (B3), 5.47 mg/L (B6), 4.04 mg/L (B7), 4.65 mg/L (B10) and 4.29 mg/L (B11). These observations suggest that the actual fluoride concentration in water from a given source is controlled by several factors reflecting both intra-formational and cross-formational heterogeneities in geological materials. These factors have varying weightings and levels of significance, but the thickness of the carbonaceous material appears to be the overriding factor.

Borehole	Total depth (aquifer thickness intersected) (m)	Total thickness of carbonaceous material (m)	% carbonaceous material to aquifer thickness intersected	Fluoride content of water (mg/L)
B7	286.51	79	27.57	2.87
B12	189.59	92.09	48.57	4.76
B6	260.3	162.3	62.38	7.26
B2	301	2002.2	66.51	5.73
B11	125.27	86	66.65	8.94
B3	121	91	75.20	7.55

Table 6.4: The influence of the percentage thickness of carbonaceous material on fluoride content of water.

Petrographic and chemical analyses are required to identify and establish the fluoride-bearing components of the carbonaceous material. From the analysis of coal-washing fractions Schultz et al. (1973) and Bouska (1981) found that in coals fluorine appears to be mainly associated with the mineral matter, particularly fluorapatite. They also pointed out that because of this, the phosphorous and fluoride contents of coals are generally positively correlated. Typical mineral matter of coal (as determined by composition of the mineral ash after combustion) consists of 0-1% phosphorous (Speight 1994), but a sample of coal from the study area contained 2.24% phosphorous (Bohmke & Duncan 1974). If the sample is representative of the coals in the area, then fluoroapatite may be a significant contributor to fluoride contamination in the water supply in the study area. Table 6.4 compares the composition of typical coal ash and that of coal ash from the study area.

Lepper (1992) reported the results of XRD analysis showing that the mineral matter of the carbonaceous mudstones and carbonaceous shales of the Lower Madumabisa Member in the study area consisted of 10-70% quartz, up to 50% kaolinite and small amounts of K-feldspar and plagioclase. Since kaolinite is thought to be an important sink for fluoride (Hounslow 1995; Ming-Ho 2000), most of the fluoride in the shales and mudstones may be contained in kaolinite. Adsorption of fluoride onto kaolinite is greatest at pH 6 and desorption, enough to significantly raise the fluoride content of water, occurs in acid ($pH<4$) and alkaline ($pH>7.5$) conditions (Hounslow 1995; Ming-Ho 2000).

Koritnig (1978) reported that in hydrothermal cycles and low temperature veins fluorite may occur in association with sulphides and barites. Most drill-hole cores of coal seams hosted in the Middle Wankie Member in the study area contained small veins or nodules of pyrite (*Report on prospecting in eastern Sebungwe* 1951). Descriptions of the pyrite are given in Appendix 5. Barites nodules were found 6 km to the NE of Sesami Mission at a locality (UTM coordinates 686098 E/ 8019433 S) within the Middle Madumabisa Member in the study area. The nodules occur at several locations on the major SE-NW trending body of the Middle Madumabisa (A. Ait-Kaci Ahmed 2002, pers. comm., 28 May). No occurrence of barites nodules has been reported within the suspected fluoride source rocks of the Lower Madumabisa Member and the Midddle Wankie Member, although their occurrence cannot be ruled out.

Constituent	**Typical Coal Ash (%)**	**Study Area Coal Ash (%)**
SiO_2	40-90	34.55
Al_2O_3	20-60	26.66
Fe_2O_3	5-25	13.47
CaO	1-15	10.49
MgO	0.5-4	1.52
Na_2O	0.5-3	1.43
K_2O	0.5-3	0.07
SO_3	0.5-10	5.61
P_2O_5	0-1	2.24
TiO_2	0-2	1.30
Cl	-	0.28

Table 6.5: Comparison of typical coal ash content (Speight 1994 p. 153), and ash content of a coal sample from the study area (Bohmke & Duncan 1974).

6.1.2 Fluoride Distribution in The Eastern Part of The Study Area

In the eastern part of the study area, a total of 23 water sources were sampled. All the water sources sit on granite or on undifferentiated 'grit, sandstone, mudstone and marl'. The lumping together of lithological units on the geological map is unfortunate as it militates against identification of the specific fluoride source units.

Figure 6.10 shows the location of all water sources in the eastern part of the study area with respect to surface geology, and the fluoride concentration of water from each source. These spatial relationships are summarized in Table 6.6.

Lithology	**Number of water sources in each fluoride concentration range**					
	0-0.5 mg/L F	0.5-1.5 mg/L F	1.5-3.0 mg/L F	3.0-6.0 mg/L F	6 0-10.0 mg/L F	Total
k	11	2	3	2	1	19
G	2	2	0	0	0	4
Total	13	4	3	2	1	23

Table 6.6: Fluoride concentrations of water from water sources in the eastern part of the study area. 'G' and 'k' under 'lithology' are explained in Figure 6.10.

The Table shows that 19 of the water sources are hosted on the undifferentiated sedimentary sequence, while only 4 are on granite. Water sources on the sediment and granite yielded water containing fluoride averaging 1.53 mg/L and 0.67 mg/L respectively. Log data (all from ZINWA) were available for only three boreholes for this part of the study area. One of the boreholes (75m deep), located on the sedimentary side of the contact with granite and which traverses sandstones with thin coal seams, yielded water (sample w224) with 2.52 mg/L F. A second borehole with log data (128m deep) is fully hosted in granite and yielded water (sample w232) of lower F content of 1.35mg/L.

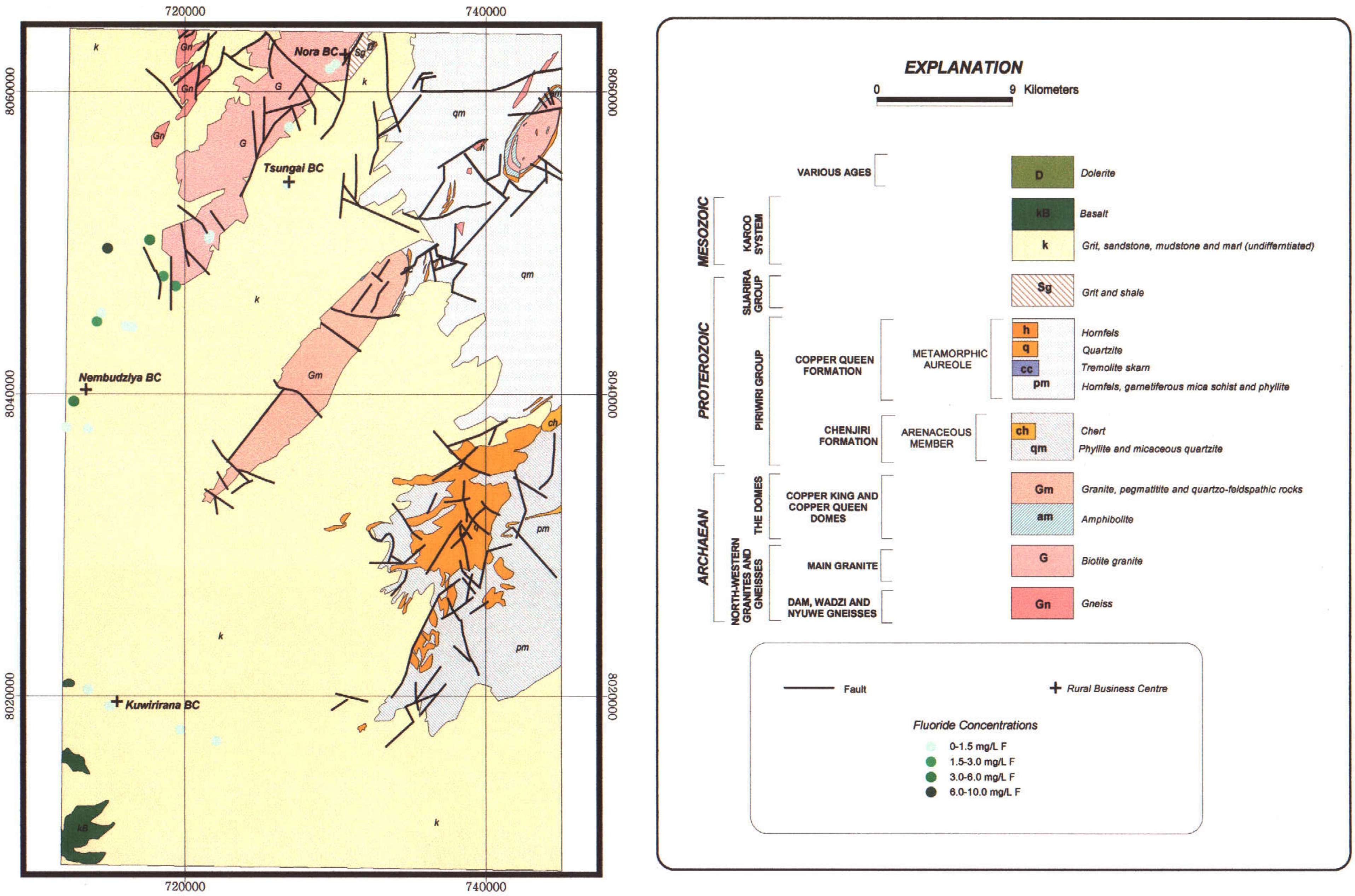


Figure 6.11: The concentrations of fluoride with respect to the location of water sources on the geological map in the eastern part of the study area. Mapped by Leyshon (1969) and degitised by Mamuse (this thesis). The grid is UTM (Zone 35).

The Middle Wankie Member, which has been shown in this study to be a potential fluoride source, is absent just east of the central part of the study area, possibly due to an unconformity at the base of the Upper Wankie Sandstone *(Report on prospecting in eastern Sebungwe* 1951; Ait-Kaci Ahmed, *in prep.)*. A third borehole, which has been logged in the eastern part of the study area, and located at Kuwirirana BC (Fig. 6.10) appears to confirm this. It is entirely hosted in sandstone, with no intervening lithological units and yielded water (sample w020) of low F content of 0.12 mg/L F.

6.2 FLUOROSIS RISK MAP

One of the major objectives of this thesis is to classify the study area into fluorosis risk zones. In this section fluorosis risk maps, based on the levels of fluoride recorded in the drinking water in the study area are developed and explained. In Table 3.1 the health effects that may stem from the ingestion of different levels of fluoride are shown. The following ranges of fluoride concentration in drinking water have been adopted in this study for the classification of possible fluorosis risk:

0-1.5 mg/L F:	No Risk
1.5-3.0 mg/L F:	Moderate Risk
3.0-6.0 mg/L F:	High Risk
6.0-10.0 mg/L F:	Very High Risk

The fluoride analysis results used in this chapter to delineate areas with of different levels of fluorosis risk are those obtained from the fluoride ion selective electrode (FISE) method (see Appendix 1).

Figures 6.12 and 6.13 are different versions of the fluorosis map of the study area. They both utilise the Inverse Distance Weighted (IDW) interpolator accessed from the Spatial Analyst Extension of ArcView® GIS software. The IDW interpolater assumes that the fluoride concentration measured at each water source applies to a certain radius around the point of measurement and this local influence diminishes with increasing distance from the point. However the two maps differ in that one is based on data from all water sources while the other utilises only borehole data. As will be discussed later, this important difference must be appreciated in any interpretation of the maps. It must also be noted that the fluorosis risk maps cover the whole of the study area including those areas for which there was no geological map.

6.2.1 Rationale, Assumptions and Limitations of Interpolation

Interpolation is used to predict unknown values for any geographic parameters such as elevation, chemical concentrations and noise levels from a limited number of sample data points where it is difficult, impossible or expensive to visit every location in the study area (McCoy & Johnston 2001). The assumption underpinning interpolation is that spatially distributed objects are spatially correlated (ESRI™ 1996; McCoy & Johnston 2001).

Deterministic interpolation methods include the IDW and Spline. How well a selected interpolation method approximates the actual situation depends on the phenomena being investigated and on how the sample points are distributed (ESRI™ 1996; McCoy & Johnston 2001). Input points can be either randomly or regularly spaced and, in general, the more numerous the input points and the greater their distribution, the more reliable the results (ESRI™ 1996; McCoy & Johnston 2001).

For this study, the IDW and Spline methods were subjected to initial comparative trials and the IDW was found to operate in a more realistic manner than Spline. The fluoride values of all points lying on the grid created by the IDW were in agreement with the values on the grid itself while for the Spline grid, this was not always the case. This failing of the Spline interpolator may be attributed to the drawback noted by ESRI™ 1996 (p.92) that, the Spline method 'is not appropriate if there are large changes in the surface within a short horizontal distance because it can overshoot estimated values'. The reliability of the IDW grid itself is not perfect because of the paucity of data points (water sources) sampled. However, the IDW interpolator appeared to work best with its parameters set to a power of 2 and a variable search radius of 3 points. The power controls the influence of known points on interpolated values and a power of 2 is most commonly used (McCoy & Johnston 2001). The number of points specified for a variable search radius corresponds to the number of points used to calculate the value of each interpolated cell. No barrier was specified.

6.2.2 Fluorosis-Risk Map Based on Data From all Water Sources

Figure 6.11 is based on the FISE fluoride concentration data from all water sources sampled in this study. The map suggests that almost half of the study area is free of fluorosis risk. The fluorosis-prone areas are quite distinct with a major occurrence to the south central portion of the study area, another towards the NE corner of the map and a lesser occurrence just to the east of the centre.

Table 6.7 gives the location of some schools, clinics and business centres in relation to the risk of fluorosis as depicted on the 'all-water sources' fluorosis risk map.

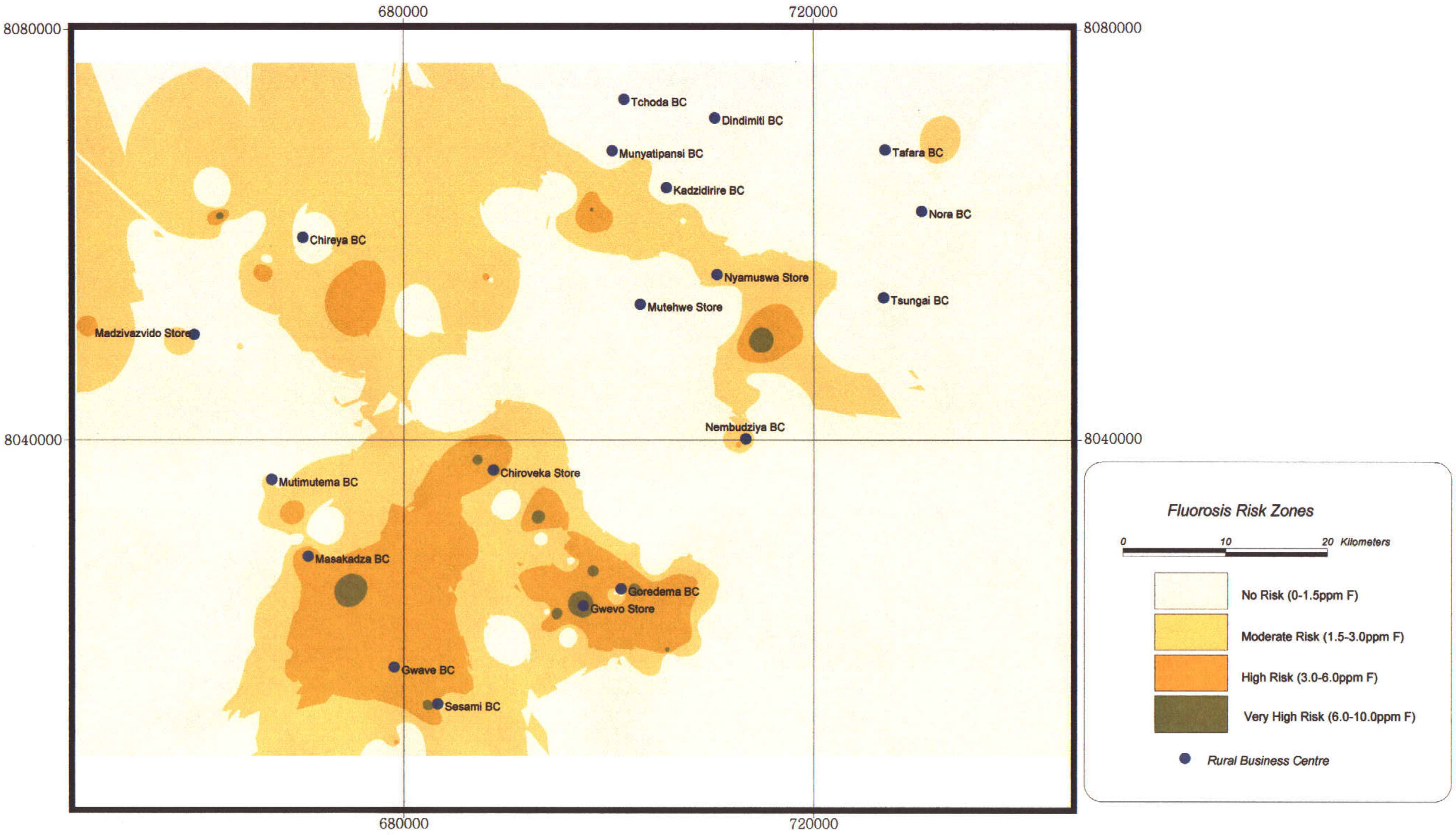


Figure 6.12: Fluorosis risk map based on fluoride concentrations from all water sources in the study area. The grid is UTM (Zone 35).

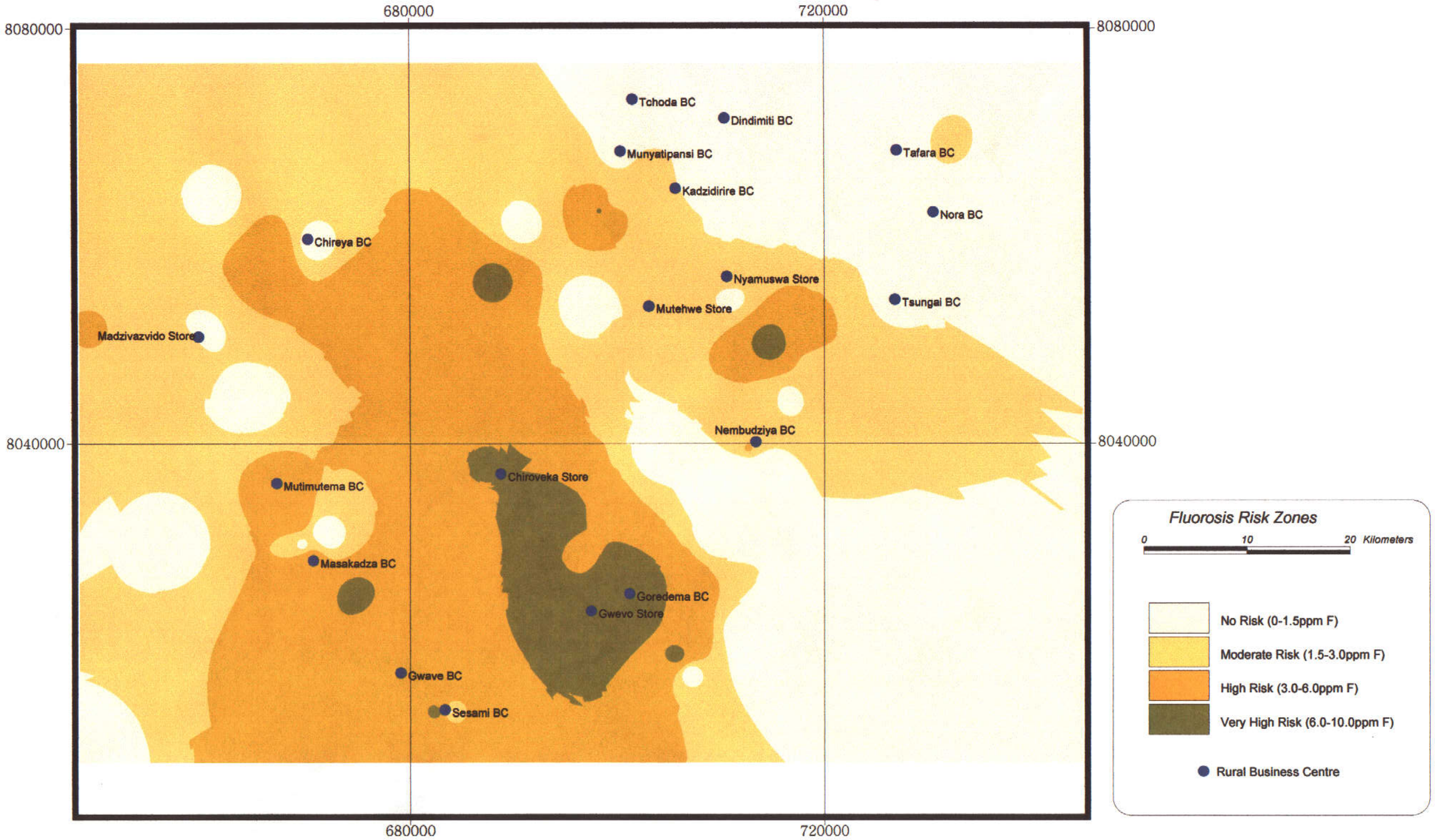


Figure 6.13: Fluorosis risk map of the study area. This map is based on the fluoride concentrations of water from boreholes (pumped and artesian) only. The grid is UTM (Zone 35).

Facility type	**Levels of fluorosis risk for each facility**			
	No Risk	*Moderate*	*High Risk*	*Very High Risk*
Primary Schools	Nyamasaka, Noname, Dindimiti, Musadzi, Mumha, Nyamhara, Dopota, Nyamuhwawo, Mpawa, Rukomo, Mtewe, St. Joseph's, Kadzidirire Dambamazura, Musosoni, Kamwembe,	Rugora,	Kajiriwanda, Umbe, Zarowa, Gwave, Mudondo,	Chomukuyu, Kahobo, Gwevo, Musorowenzou Goredema,
Secondary Schools	Mbovhana, Svibe, St. Joseph's		Nemangwe	Gurawakanya
Clinics	Chireya, Madzivazvido	Rupenyu, Sesami Mtora, Msita		Denda Kahobo, Goredema
Business Centres	Nora, Mtewe Chireva, Tsungai, Munyatipansi Tafara, Kadzidirire Madzivazvido	Nebudziya, Nyamuswa, Mutimutema,	Chiroveka, Masakadza, Gwave, Sesami	Goredema Gwevo

Table 6.7: Location of key facilities with respect to the fluorosis map based on all water sources.

6.2.3 Fluorosis-Risk Map Based on Borehole Data Only

Figure 6.12 shows the fluorosis map for the area of study based on data obtained from pumped and artesian boreholes only. Broadly, the map consists of asymmetric zones of decreasing fluoride levels away from the Goredema-Denda-Kahobo area in all directions. The total area covered by the 'very high-risk' zone is up to 200 km^2 and it is mainly distributed around the Goredema area. Three isolated circular 'very high-risk' zone patches ranging in area between 7 km^2 and 11 km^2 occur around Kamhororo (27 km west of Goredema Clinic), Chomukuyu Primary School (32 km NNW of Goredema Clinic) and Musorowenzou Primary School (28 km NE of Goredema Clinic). There are other smaller patches of the zone such as just to the west of Sesami Mission and to the SW of Mudondo School. A much larger (about 1 200 km^2) 'high-risk' zone envelops the 'very high-risk' zone and it is in turn enclosed by the 2 250 km^2 'moderate-risk' zone. A 2 350 km^2 'no-risk' zone occurs mainly to the west of the study area and also as sporadic patches within the 'moderate-risk zone'.

Table 6.8 indicates the location of some of the major facilities and service centres in the study area in relation to the fluoride data from boreholes only.

Facility type	**Levels of fluorosis risk for each facility**			
	No Risk	*Moderate Risk*	*High Risk*	*Very High Risk*
Primary Schools	Nyamasaka Noname, Dindimiti, Musadzi Mumha, Nyamhara, Dopota	Nyamuhwawo, Mpawa Rukomo, Mtewe, St Joseph's, Kadzidirire Dambamazura,	Musosoni, Kajiriwanda, Umbe Zarowa, Gwave, Mudondo, Kamwembe, Rugora,	Chomukuvu Kahobo, Gwevo, Musorowenzou Goredema,
Secondary Schools	Mbovhana,	Svibe, St. Joseph's	Nemangwe	Gurawakanya
Clinics		Chireya, Madzivazvido	Rupenyu, Sesami Mtora, Msita	Denda, Kahobo, Goredema
Business Centres	Nora, Chireya, Tsungai, Munyatipansi, Tafara, Madzivazvido	Nebudziya, Nyamuswa, Mtewe, Kadzidirire	Masakadza, Gwave, Mutimutema, Sesami	Chiroveka, Goredema, Gwevo,

Table 6.8: Location of key facilities with respect to the fluorosis map based on fluoride data from boreholes only.

6.2.4 Differences Between The Two Maps

6.2.4.1 Visual Appearance

The fluorosis maps shown in figures 6.11 and 6.12 visually appear different in terms of the distribution of fluorosis risk zones. This implies that the same pieces of ground may be designated into different fluorosis risk zones if the maps are compared. As an illustration of this, Table 6.9 compares the fluorosis risk location of the facilities in Table 6.7 and Table 6.8. From Table 6.9, it is clear that overall, the map based on all water sources is a 'dilute' version of the boreholes-only map; it generally downgrades fluorosis risk designation and creates a less acute picture. However for some areas the maps suggest the same fluorosis risk classification.

Type of facility	**Name of facility**	**Comparative fluorosis risk designation**	
		Figure 6.11 (all watersources)	Figure 6.12 (boreholes only)
Primary Schools	Nyamasaka, Noname, Dindimiti, Musadzi, Mumha, Nyamhara, Dopota	No risk	No risk
	Nyamuhwawo, Mpawa, Rukomo, Mtewe, St Joseph's, Kadzidirire, Dambamazura	No Risk	Moderate Risk
	Musosoni, Kamwembe	No Risk	High Risk
	Rugora	Modertae Risk	High Risk
	Kajiriwanda, Umbe, Zarowa, Gwave, Mudondo	High Risk	High Risk
	Chomukuyu, Kahobo, Gwevo,Musorowenzou, Goredema	Very High Risk	Very High Risk
Secondary Schools	Mbovhana	No Risk	No Risk
	Svibe, St Joseph's	No Risk	Moderate Risk
Clinics	Chireya, Madzivazvido	No Risk	Moderate Risk
	Rupenyu, Sesami, Mtora, Msita	Moderate Risk	High Risk
	Denda, Kahobo, Goredema	Very High Risk	Very High Risk
Business Centres	Nora, Chireya, Tsungai, Munyatipansi, Tafara, Madzivazvido	No Risk	No Risk
	Mtewe, Kadzidirire	No Risk	Moderate Risk
	Nembudziya, Nyamuswa	Moderate Risk	Moderate Risk
	Mutimutema	Moderate Risk	High Risk
	Masakadza, Gwave, Sesami	High Risk	High Risk
	Chiroveka	High Risk	Very High Risk
	Goredema, Gwevo	Very High Risk	Very High Risk

Table 6.9: Comparison of the location of key facilities on 'all water sources' fluorosis map and on 'boreholes-only' fluorosis map.

6.2.4.2 Interpretation, Limitations and Applications

The map in Figure 6.11 which is based on all types of drinking water sources in the study area, may be a useful tool in contemporary studies focussing on human fluoride exposure, but it has limited application in planning groundwater resource development in the area. This is because a large number of shallow (commonly >1m) water sources tapping water from superficial deposits is included in the classification. The shallow sources are seasonal phenomena and represent undeveloped groundwater resources. Consequently, water samples from such sources are not representative of the groundwater quality of the area.

On the other hand Figure 6.12, which uses only fluoride data from pumped boreholes and artesian boreholes provides a more reliable water resources planning tool because borehole development appears to be one of the most viable options for the long-term water needs in the area. Already, most major service centres such as schools, clinics and business centres utilise borehole water and overall, boreholes (pumped and artesian) constitute more than half of the water sources sampled. Furthermore, most people in the area will be reliant upon boreholes in the drier season when the shallow sources dry up. It is also likely that if only borehole data are used in fluorosis risk classification a more reliable relationship between geology and water chemistry may be reflected on the map because boreholes in the area generally penetrate beyond superficial material.

6.2.5 The fluorosis Risk Map: Implications for Health

Tobayiwa et al. (1991) reported that the prevalence of dental fluorosis among examined school children of five schools in Gokwe was 61.9%. Using the TF index, they found that the prevalence of severe fluorosis (TF>4) was 20.4 %. Included in the survey were Goredema Primary School, Gwevo Primary School and Umbe Primary School. According to the fluorosis map of the present study, Goredema and Gwevo schools lie in the 'very high risk' zone while Umbe sits on the 'high risk zone'. The other two schools surveyed by Tobajwa et al. (1991) lie outside the present area of study.

In this study a fluorosis survey was not undertaken but many individuals, particularly children, with disfigured teeth were observed. From informal interviews with the people, it was evident that they knew that it was the water they consumed that was responsible for the problem. Photographs on the frontispiece of this thesis show some signs of fluorosis in individuals in the study area. A nursing assistant at Kahobo Clinic mentioned that the clinic attends to many children from Kahobo and Umbe primary schools with limb fracture complaints, resulting from sporting or falling accidents. He said the clinic staff considered the occurrences unusual and they thought they emanated from the consumption of 'poisonous' water.

Adherence to the 1.5 mg/L WHO (1984; 1996; 2000) guideline value of fluoride in drinking water does not universally guarantee protection against fluorosis. For example, Warnakalusuriya (1992) reported that among villagers drinking water containing less than 1.0 mg/L fluoride in Sri Lanka, 32% of the children had mild forms of dental fluorosis and 9% severe forms. From this work it was recommended that the WHO upper limit for fluoride in drinking water in hot dry climates, where more water is likely to be consumed, should be set at 0.8 mg/L. In a large scale survey carried out in China, Chen et al. (cited in *Fluoride*, no date) found that dental fluorosis was detectable in 46% of the population consuming water with 1mg/L fluoride. The implication of these observations is that in Gokwe, which has a hot dry climate, dental fluorosis cases may occur in the 'no risk zone' of the fluorosis map. It must also be noted that the zone has been designated 'no risk' with respect to fluorosis only. Ninety-nine of the 149 (66.44%) of the water sources sampled in the 'no risk' zone yielded water with less than 0.5 mg/L F. Such fluoride-deficient water can expose the population to dental caries (Edmunds & Smedley 1996).

According to WHO (1996), in temperate climates skeletal fluorosis can occur among people who drink water containing 3-6 mg/L fluoride, and at lower concentrations in hot dry climates. It has been suggested that relatively low levels of fluoride in drinking water (1-4 mg/L) may be associated with bone fracture (e.g. Sowers et al. 1991; Danielson et al. 1992), although other studies, have established a weak or no correlation between fluoride concentration in drinking water and the incidence of bone fracture (e.g. Madans et al. 1983; Cauley et al. 1995; Arnala et al. 1996; Hillier et al. 2000). The incidences of limb fracture reported among Umbe and Kahobo school children in the current study may be the signs of skeletal effects of fluorosis.

Crippling skeletal fluorosis is thought to develop in people who have ingested 10-20mg (equivalent to about 10 mg/L F in drinking water) of fluoride per day for 10-20 years (NRC 1993; WHO 1996; 2000). However in a study in Senegal, Brouwer et al. (1988) found that of the 42 individuals who had consumed drinking water with 7.4 mg/L fluoride, 11 (26%) had developed skeletal fluorosis. It is therefore likely that the fluoride concentrations necessary for crippling skeletal fluorosis to develop exist in Gokwe, particularly in the 'very high risk' zone. However, such cases may only be starting to emerge now because the area was settled relatively recently. By the 1980s, people were still moving into the area following the successful eradication of tsetse fly in the mid 1960's.

Taking these observations into account, the fluorosis map may be interpreted as shown in Table 6.10.

Fluorosis zone	**F concentration**	**Possible health risk**
No risk	0-1.5 mg/L	Dental caries mild dental fluorosis (low prevalence)
Moderate risk	1.5-3.0 mg/L	Moderate dental fluorosis fracture incidences
High risk	3.0-6.0 mg/L	Severe dental fluorosis bone fracture incidences, skeletal fluorosis
Very high risk	6-10 mg/L	Severe dental fluorosis bone fracture incidences, skeletal fluorosis, crippling skeletal fluorosis

Table 6.10: Possible maladies associated with the proposed fluorosis-risk zones.

If the foregoing is correct, many implications arise. Gokwe is a relatively large district with a population of nearly 200 000 people. It is already known that dental fluorosis and severe dental fluorosis are highly prevalent in the district. It is likely that cases of skeletal and crippling skeletal fluorosis may be starting to emerge as people in the area have now been exposed to excessive fluoride for long enough. Gokwe is the largest cotton-producing district in Zimbabwe, and it is also a major beef producer. In Gokwe, both activities are labour-intensive and younger farmers may currently be gradually taking over from their older parents. These younger farmers, most born in Gokwe, have been exposed to fluoride throughout childhood and adolescence. A generation of crippled farmers may be in the offing. Cattle are also known to succumb to fluorosis, and this can potentially cripple economic activity in Gokwe further. The following quotation, from a fluorosis researcher, Eli Dahi spells out the perilous impact of crippling skeletal fluorosis on humans:

> "The farmer with black teeth seemed fine the first time I saw him-out all day working. I know that he carried on drinking the same fluoride-rich water he had drunk since he was born Five years later when I returned to the village his legs had buckled under him. He was practically a cripple. I don't know what he did for a living" (Dahi cited in *Where we need to act 2001*, p.2).

6.3 MAJOR IONS AND TDS

The focus this study has been to investigate the distribution and concentration of fluoride in the drinking water supply of Gokwe District and to spell out the associated health effects. However it is known that the concentration of free fluoride ions in water, and thus the bioavailability of F^-, may be affected by the presence of other ions. This section discusses the occurrence of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} in the water supply of the study area, with respect to TDS and fluoride contamination. Possible health impacts of different concentration levels of these ions in community water supplies are also considered.

Table 5.2 in Chapter 5 shows the concentrations of the major ions and TDS with respect to WHO guidelines for drinking water quality. All the WHO guidelines given in Table 5.2 are aesthetic limits except nitrate for which a health limit of 50 mg/L is suggested. For sodium, WHO (1993) suggested an aesthetic limit of 200 mg/L, but DEP (2001) indicated that at concentrations greater than 60 mg/L, sodium aggravates sodium sensitive hypertension and diseases that cause difficulty in regulating body fluid volume.

Although attention must also be given to aesthetically displeasing water sources, sources with water that exceed health guidelines are of more immediate concern. In this regard, the health-based water quality standards developed for South Africa by CSIR (1991) are adopted here to classify the water supply in the study area (Table 6.11).

Parameter (mg/L)	No risk range	Low risk range	High risk range
Cl^-	0-600 (123)	600-1200 (4)	>1200 (2)
NO_3^{2-}	0-50 (122)	50-100 (3)	>100 (4)
SO_4^{2-}	0-600 (123)	600-1200 (6)	>1200 (0)
Na^+	0-400 (117)	400-800 (10)	>800 (2)
K^+	0-400 (129)	400-800 (0)	>800 (0)
Mg^{2+}	0-100 (125)	100-200 (3)	>200 (1)
Ca^{2+}	0-200 (127)	200-400 (0)	>400 (2)
TDS	0-1500 (118)	1500-2000 (0)	>2000 (11)

Table 6.11: CSIR (1991) guidelines for domestic water supply. The number of water sources in the study area that fall in each health risk range is shown in parenthesis.

Table 6.11 shows that at least 90% of the samples fall in the "no risk" range for all the parameters determined. A few samples that fall in the medium or high-risk range, particularly for TDS, Na^+, NO_3^{2-}, may raise some health concerns. Figures 6.14 and 6.15 show simple chemical trends of individual ionic species vs. TDS. The clear positive correlation of sodium and chloride with TDS (quantified in Figure 6.16) suggests that the two contribute significantly to the bulk of TDS in the water supply of the study area. The areal distribution trends of sodium and TDS for the area are depicted in Figure 6.17. Generally, water in the study area with TDS of at least 2000 mg/L has an unpleasant salty taste and is no longer widely used as drinking water. However it continues to be used for washing and watering gardens and livestock. Samples of this excessively salty water collected for the present study include w198 (deep well, 14750 mg/L TDS, 3468 mg/L Na^+), w059 (artesian borehole, 3210 mg/L TDS, 478 mg/L Na^+) and w055 (artesian borehole, 3180 mg/L TDS, 796 mg/L Na^+).

The insert in Figure 6.18 encompasses the Bari Salt Pan, a locality where table salt and a vegetable and meat tenderiser (possibly trona, $Na_3H(CO_3)_2.2H_2O$) are extracted by local villagers from soils. The salts may have emanated from saline waters channelled to the surface along faults. Ait-Kaci Ahmed (in prep.) reported the presence of numerous faults with a total upthrow of 50 m over 1 km at Bari Salt Pan. It is thought that such saline waters originate from the dewatering of sedimentary basins (Davis & DeWiest 1966; Maynard 1991). The consumption of high-fluoride trona has contributed significantly to the prevalence and severity of fluorosis in Tanzania (Mabelya et al. 1997). Analyses of the salts from the Bari Salt Pan (Table 5.3, Chapter 5) indicate that they both contain elevated levels of fluoride. In addition most water boreholes around the Bari Salt pan issued salty high-fluoride water. In contrast, Figure 6.18 suggests that TDS and its main constituents, Na and Cl, generally correlate poorly to F in the water supplies of the study area.

However, when the data are grouped (Tables 6.12 and 6.13) and plotted (Figures 6.19 and 6.20), hidden relationships between concentrations of different ions and TDS emerge. In Table 6.12, water samples collected from the study area are grouped into 3 arbitrary TDS ranges, namely 0-500 mg/L, 500-1000 mg/L and 1000-5000 mg/L (The 5000 mg/L maximum has been chosen to exclude an outlier sample (w0198, 14750 mg/L TDS). The arithmetic mean of the concentration of each ion in samples corresponding to each TDS range was calculated and plotted against TDS (Fig. 6.19). Average concentrations of F and Ca (Fig. 6.19a), and Cl, NO_3, SO_4 and Na (Fig. 6.19b) all positively correlate with TDS. K (Fig. 6.19a) has a pronounced negative correlation with TDS, whereas Mg (Fig. 6.19b) has a higher value in the middle TDS range and lower values at high and low TDS ranges.

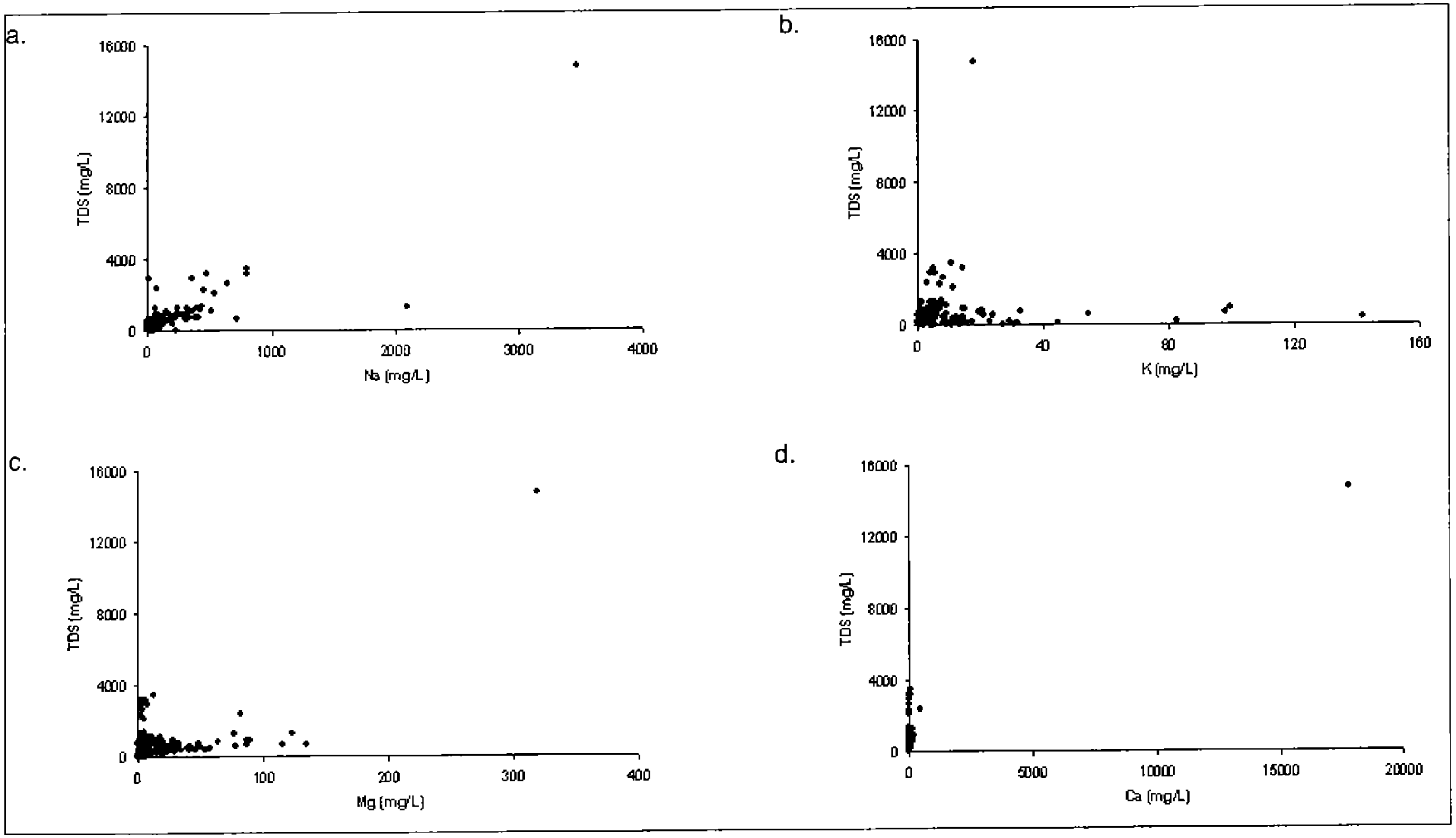


Figure 6.14: Plots of cations vs. TDS of water supplies in the study area.

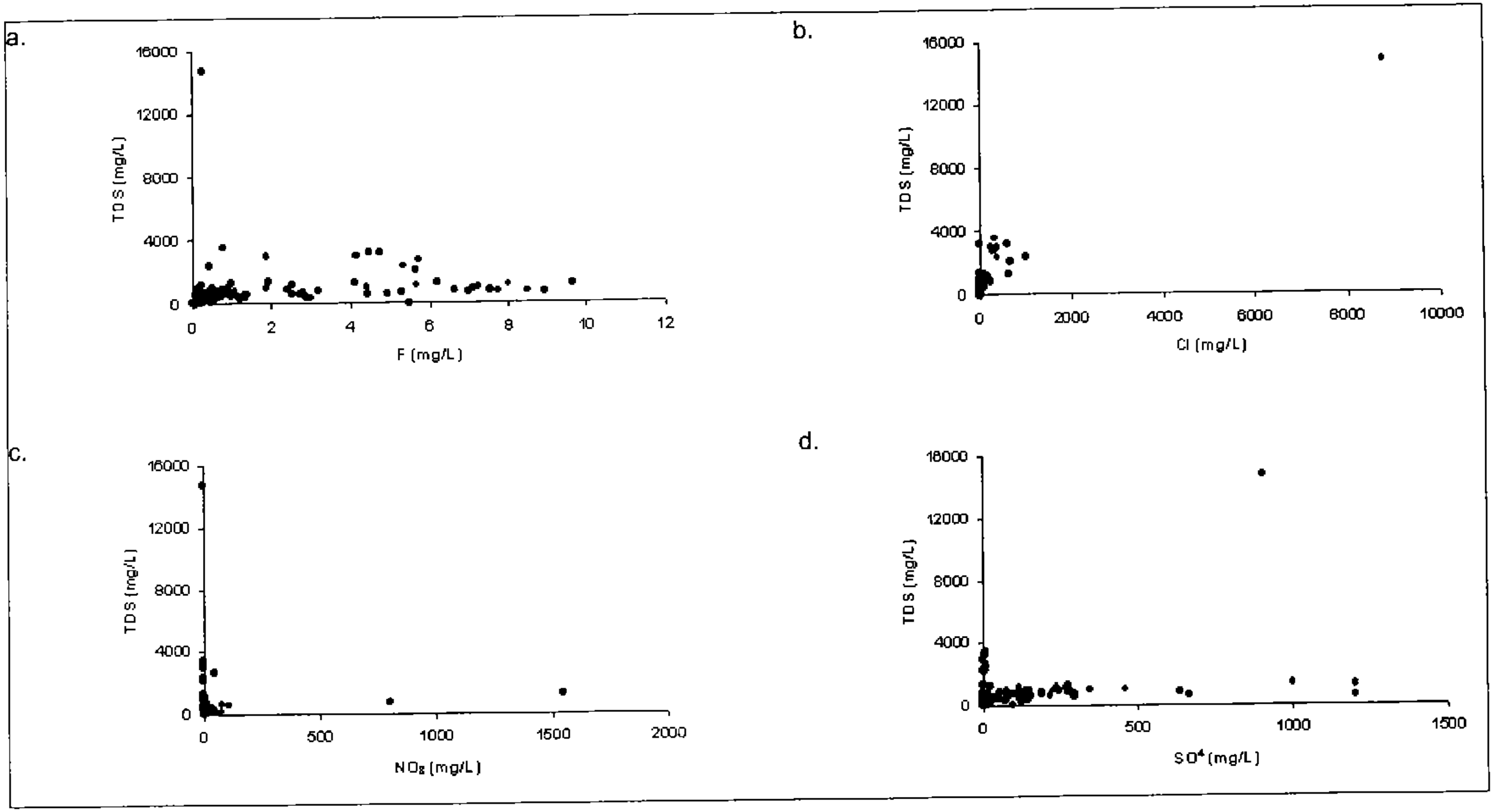


Figure 6.15: Plots of anions vs. TDS of water supplies in the study area

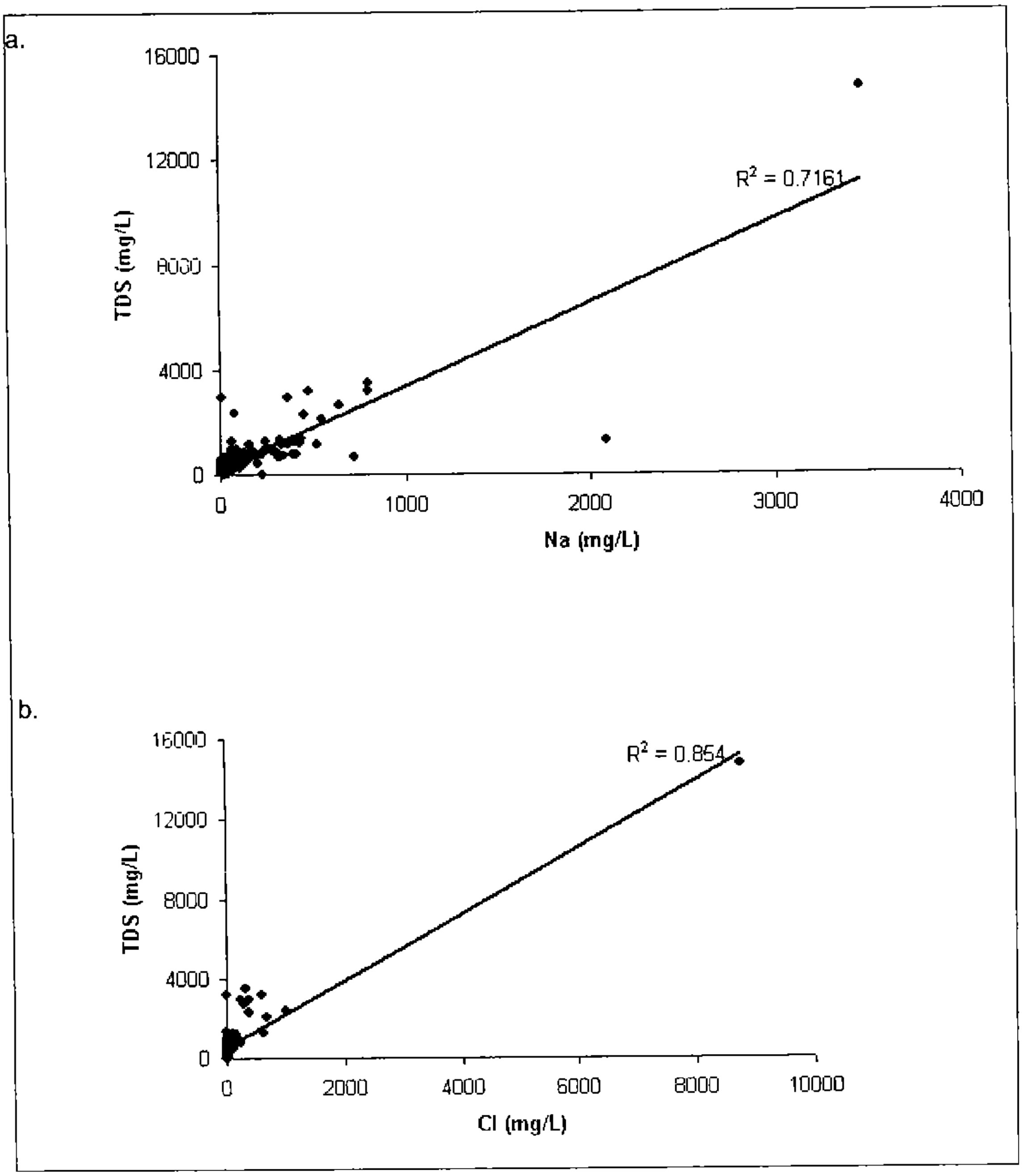


Figure 6.16: Correlations of Na and Cl with TDS in water supplies of the study area. The strong positive correlations suggest that Na and Cl contribute significantly to the TDS of water in the area.

Figure 6.17: Variation of TDS (contours) and sodium (green symbols) in the study area. The insert zooms in on the area of very high sodium concentrations. The grid is UTM (Zone 35).

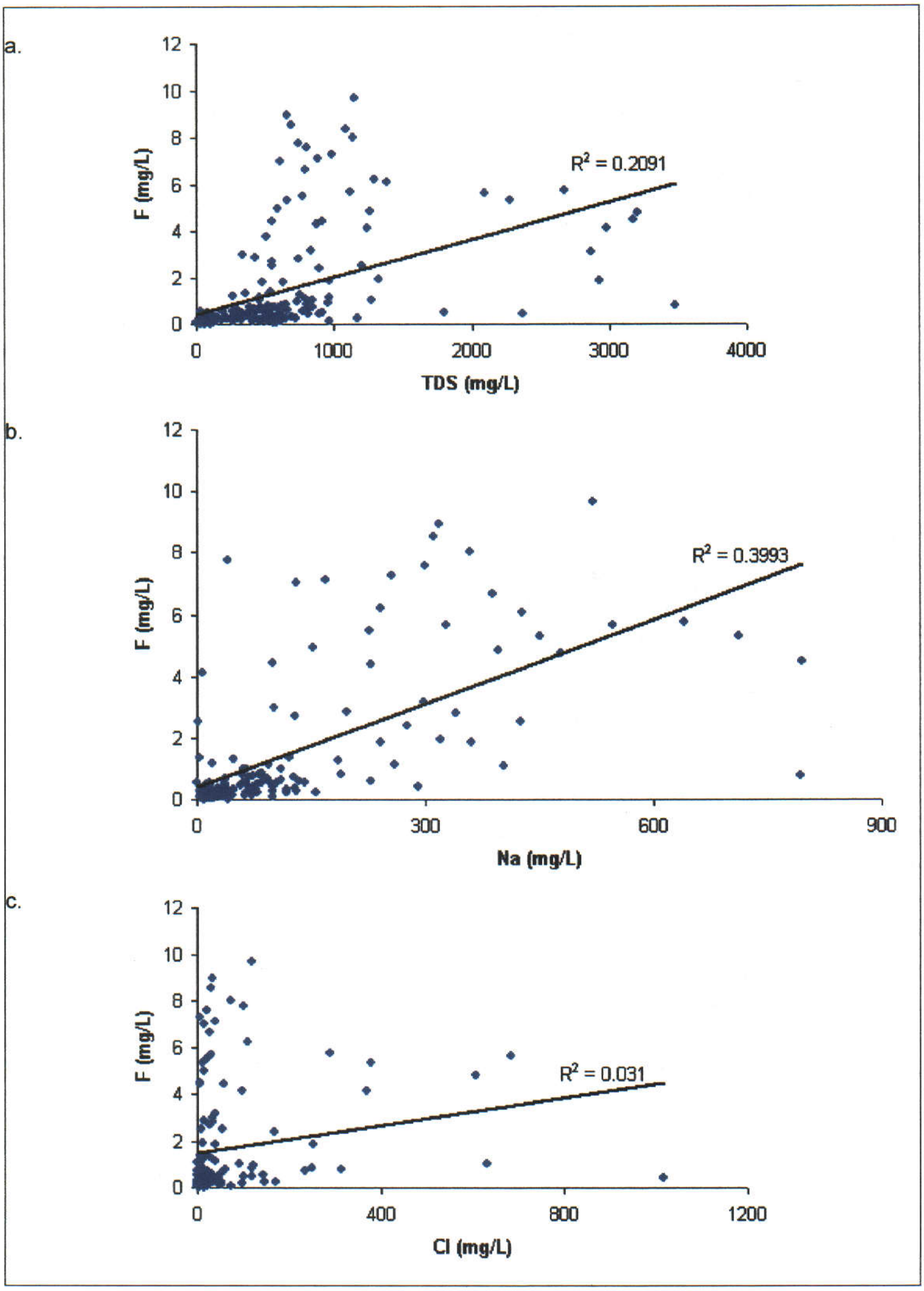


Figure 6.18: Plots of TDS, Na and Cl against F. The poor correlations may be misleading as shown by further processing (grouping) the data. See text for details.

TDS range (mg/L)	Average concentration of determinands in mg/L								Number of water source types with samples in each TDS range							
	F	Cl	NO_3	SO_4	Na	K	Mg	Ca	BOR	ATE	DWE	SWE	DAM	SPN	RVB	RIV
0-500	0.44	15.00	10.71	54.57	44.38	12.34	11.78	12.10	31	1	24	22	6	2	9	4
500-1000	1.99	49.43	19.68	129.04	153.86	9.74	28.32	28.73	34	6	12	3	0	1	9	3
1000-5000	4.17	326.40	92.04	171.86	461.12	6.29	18.20	39.32	13	9	4	0	0	0	1	0

Table 6.12: Average concentrations of ions of water samples within each TDS range. The water sources are: BOR (pumped boreholes), ATE (artesian boreholes), DWE (deep wells), SWE (shallow wells), DAM (dams), SPN (springs), RVB (riverbed wells), and RIV (rivers).

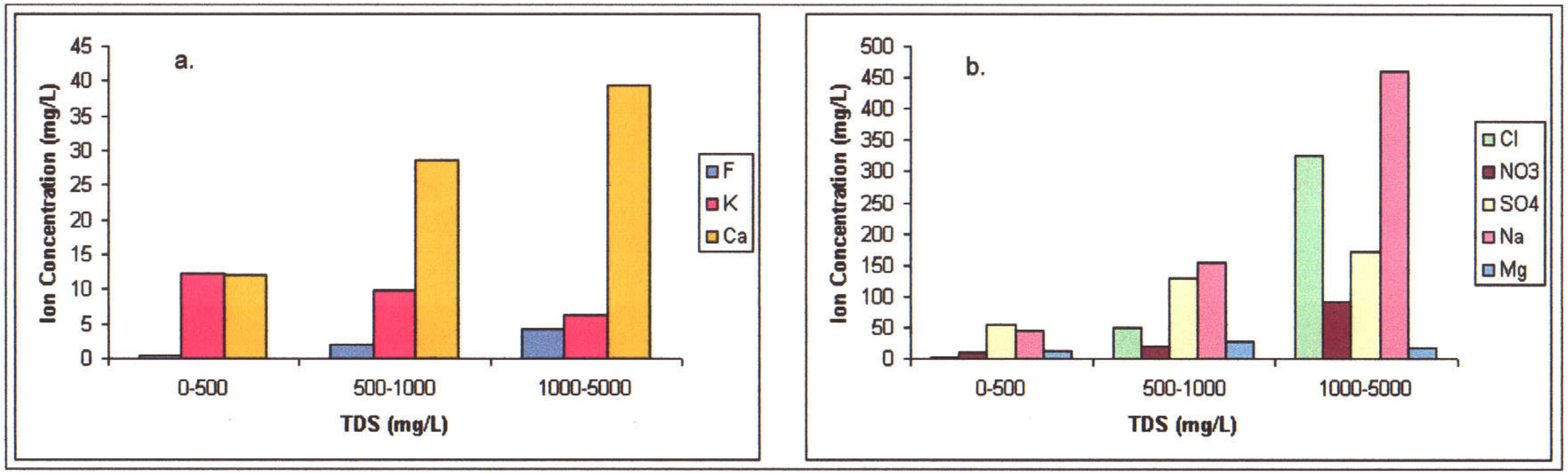


Figure 6.19: Relationships between TDS and the average concentrations of individual ions in the water supply of the study area.

In Table 6.13 the concentrations of other determinands of water samples of the area have been grouped according to the fluoride contents of the samples. The fluoride concentration ranges used have been adopted from the fluorosis risk classification used in section 6.2. The average concentration of each ion and TDS of samples containing fluoride within each range concentration range was plotted against this range (Figure 6.20). It has been necessary to plot three graphs because of the wide variation on the vertical scale. It appears that where waters range in F content between 0 and 6mg/L F, higher average Na (Fig. 6.20a) and TDS (Fig. 6.20c) contents are associated with the higher end of the F range. Figures 6.20a and 6.20c show that this trend is not maintained as samples with F contents in the range 6-10 mg/L register lower average Na and TDS contents compared to those containing 3-6 mg/L F. Peak Cl and SO_4 concentrations are attained in waters containing F in the range 1.5-3 mg/L and fall below and above that F range (Fig 6.20a). Figure 6.20b shows that the concentrations of Mg and NO_3 are negatively related to the F contents of waters in the study area. Ca (Fig. 6.20a) shows a similar but less pronounced relationship with F.

F range (mg/L)	**Average concentration of determinands in mg/L**							
	Cl	NO_3	SO_4	Na	K	Mg	Ca	TDS
0-1 5	[illegible]	31 67	76.71	100 76	10.15	23.92	183.92	547 355
1.5-3 0	[illegible]	22 8	217.73	250 21	9 19	21.46	15.94	1230 923
3.0-6 0	165.97	3.12	149.99	462 7	10.87	13.17	20.94	1458 793
6 0-10 0	52.55	0 65	149.44	288 4	4 16	2.98	4 54	1188.857

Table 6.13: Average concentration of ions in water samples grouped by fluoride concentration range of the samples.

6.4 FLUORIDE AND PH

Alkaline waters are commonly high in fluoride because of fluoride desorption from kaolinite in reverse anion exchange that occurs in waters with pH>7.5 (Hounslow 1995; Ming-Ho 2000). Figure 6.20 shows the relationship between the pH of water in the study area and its fluoride content. A plot of all the samples (Fig. 6.20a) suggests a hazy positive correlation between the two, which disappears when outlier samples are discarded (Fig. 6.20b). However, from Figure 6.20c, it is clear that moderately alkaline waters (pH 7.8-9) are associated with high levels fluoride contamination. The pH ranges used in the graph were adopted from the classification of Hounslow (1995). He classified geochemical environments into strongly acid (pH<4), moderately acid (pH 4-6.5), neutral (pH 6.5-7.8), moderately alkaline (pH 7.8-9) and strongly alkaline (pH≥9) types. The inclusion of the strongly alkaline sample in the graph is somewhat misleading because the sample was obtained from a deep well a few hours after construction. The well still had fresh cement-and-brick lining and the alkalinity, not reflected in an older adjacent well, is likely to have been a temporary phenomenon emanating from the carbonate constituent of cement mortar.

6.5 MAJOR IONS, TDS, PH AND F CONTAMINATION: A SYNOPSIS

From Section 6.3, TDS and several ions appear to influence the concentration of F in water supplies in the study area. In Figure 6.19a average F concentrations increase with increasing TDS, which has been shown to be closely associated to Na and Cl concentrations (Fig. 6.16). Strubel (cited in Koritnig 1978) showed that adding successively higher amounts of NaCl to water could increase the solubility of fluorite, CaF_2. While the mineral fluorite has not been found in the area, the occurrence of sulphides and barites, minerals commonly associated with low temperature fluorite veins (see Section 6.1.1.4), has been reported. Therefore salt-containing groundwater in the area may have increased local fluoride content in the water supply by more strongly leaching out fluoride from fluorite or other F-bearing aquifer materials. However waters with the highest range of F concentration in the study area (6-10 mg/L) are not associated with the highest TDS (or Na and Cl) concentrations (Fig. 6.20a,c). Rather the highest TDS and Na concentrations are attained in waters with F concentrations in the range 3-6 mg/L. This suggests that other factors may be more dominant in controlling F availability than NaCl-controlled solubility of F-bearing materials under certain conditions. The existence of F-bearing materials whose solubility may not be NaCl-controlled could be an important factor. Other F-bearing materials possibly occurring in the geological materials of the area include fluorapatite and kaolinite (Section 6.1.1.4) and trona ($Na_3H(CO_3)_2.2H_2O$).

The highest F concentrations are not associated with highest TDS and NaCl concentrations (Section 6.3) but with moderately alkaline conditions (Section 6.4). This suggests that pH may be the more dominant factor than NaCl-controlled availability of F in environments of the study area where F contamination of groundwater is greatest. If this is correct then, from Section 6.4, kaolinite could be an important, if not the major, contributor to F contamination in the worst affected parts of the study area. In other environments F-bearing trona may be a significant F source, particularly in areas where it is abundant enough to be harvested for consumption (see section 5.4, Chapter 5).

Figure 6.20b reveals a strong negative correlation between Mg and F concentrations in water supplies, whereas in Figure 6.20a the well-known (Handa 1975; Hem 1985; Edmunds & Smeldley 1996) general negative correlation between F and Ca concentration in natural waters is less convincingly displayed. Is it, therefore, that the precipitation of sellaite (MgF_2) is an important factor in fluoride availability in the water supplies?

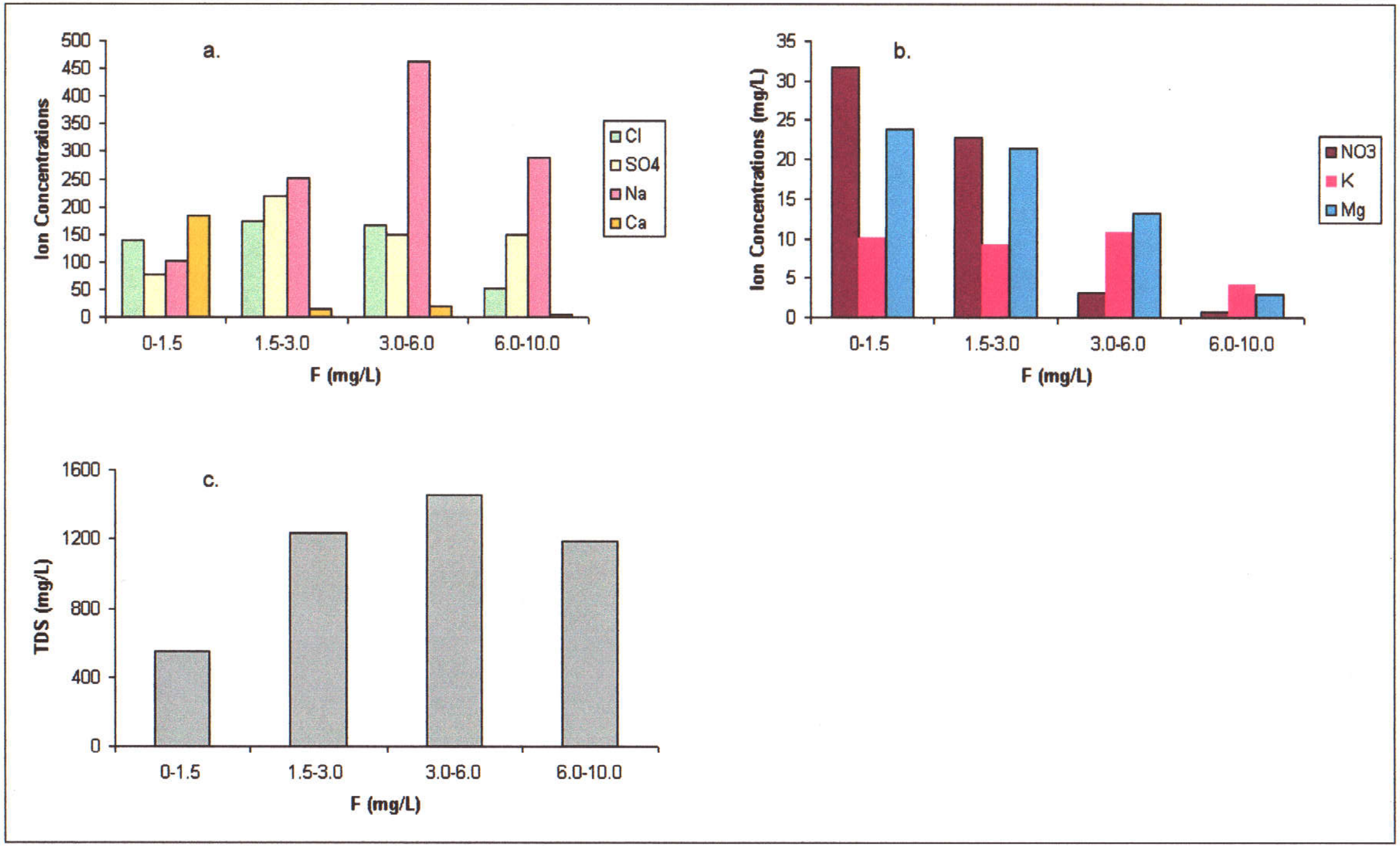


Figure 6.20: Average concentrations of TDS and certain ions vs. F concentration.

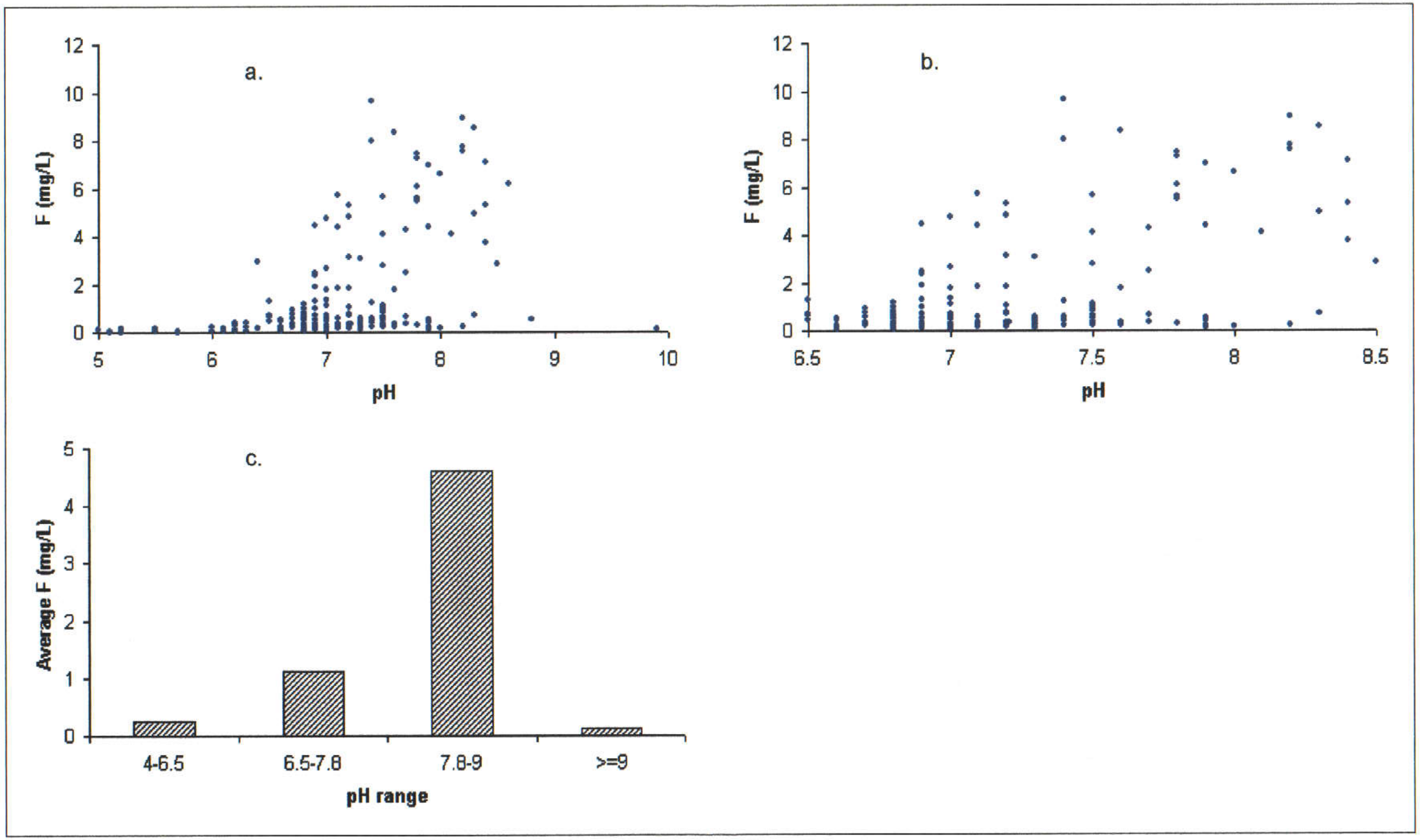


Figure 6.21: Plots of pH vs. F values in water samples from the study area. See text for explanation.

7

RECOMMENDATIONS AND CONCLUSIONS

7.1 REMEDIAL METHODS

The implications of fluorosis in Gokwe described in section 6.25 suggest a bleak future for the population unless measures can be implemented to mitigate the impact of fluoride toxicity. Measures include avoiding fluoride-rich water, and fluoride removal technologies (defluoridation).

7.1.1 Avoiding Fluoride-rich Water

Fluoride-rich water can be avoided if experience and/or area-specific hydrogeological expertise are judiciously applied in the siting and construction of water sources. Shallow water sources in the study area generally contained acceptable fluoride concentration levels (see Chapter 5). Therefore, the risk of fluoride exposure can be minimised if villagers in areas with fluoride-contaminated groundwater are encouraged to utilise, where available, water from shallower sources (shallow wells, dams, streams) rather than water from boreholes or deep wells. Installers of drinking water facilities must be advised only to drill boreholes where it is not sustainable to utilise shallower water sources. In several villages in the study area, adults were reserving scant fluoride-free water collected from shallow river-bed wells for young children while they continued to consume the more abundant fluoride-rich borehole water. The effectiveness of this strategy is limited because in drier seasons, the shallow sources dry up, forcing the children to drink the only water available - the fluoride rich borehole water.

Another measure to avoid excessive fluoride involves sinking boreholes in places where the geological formations responsible for fluoride contamination are absent. The strategy seems attractive for populations on the moderate risk zone in villages to the east of Goredema BC (business center) and at Nembudziya BC and surrounding villages (Fig. 6.13). The benefit of this strategy to Nembudziya BC is of particular interest because the business centre is fast growing and may be upgraded to a town in the near future. Nembudziya, which is run by a council, is electrified and has a residential area of planned housing receiving council-supplied tap water sourced from two boreholes. Other facilities include a hospital, a government office complex (including ministries of water development, education and agriculture), primary and secondary schools, several lodges, nightclubs, a police station, a cotton marketing deport, several canteens, a cultural centre and a community library. The two boreholes that supply water to Nembudziya are 5.76 km apart (Fig. 6.11) and yielded water with 3.19 mg/L F (southerly borehole in high risk zone on Fig. 6.13) and 2.80 mg/L F (northerly borehole in moderate risk zone on Fig. 6.13) respectively. The shortest distance from the southerly borehole to the 'no risk zone' to the south is 920 m and the northerly borehole is situated 1.43 km to the west of the nearest low risk zone. It appears therefore that the high-fluoride waters are localized. These scenarios suggest that the large population of Nembudziya BC can be spared the worst effects of fluorosis if new water supply boreholes are installed in the adjacent 'no risk areas' to replace the high fluoride boreholes currently in use. Low fluoride water is available in the low fluoride zones, both within 1.9 km from the Nembudziya's northerly and southerly boreholes (see Fig.6.11). For example, two boreholes to the east of the northerly borehole (Fig. 6.11) yielded water containing 0.49 mg/L F (sample w221) and

0.44 mg/L F (sample w222 mg/L F). Two boreholes to the south of the southerly borehole (Fig. 6.11) yielded water with 0.34 mg/L F (sample w153) and 0.21 mg/L F (sample w154). Before implementing this proposed solution, more information about the depths and log data of the boreholes in the favourable locations must be considered and fully understood and stratigraphic correlations checked against the conditions at the current borehole locations. In addition, research must be undertaken to investigate the effects of new boreholes on the hydrogeological regime. For example, over-pumping, may lead to permanent aquifer damage or modification of groundwater flow. A further option available for Nembudziya is to rehabilitate and utilize Maselukwe Dam, which lies 600 m from the northerly borehole. The plausibility of this option depends on the dam's storage capacity vis-à-vis Nembudziya's water requirements.

Another way to avoid fluoride-rich water in the area is to determine optimal depths for boreholes, depths that ensure sufficient supply of water without having to drill unnecessarily deep, as chances of fluoride contamination appear to increase with depth. In a way, the discovery of the artesian system in Gokwe during exploration of coal in the 1950's set a bad precedent because most villagers now crave for artesian water because it is plentiful (so it can additionally be used for watering livestock and gardening) and requires no pumping expense and effort once it is found. In one village, farmers who had hoped to strike artesian water refused to pay back their borehole drilling loans when artesian flow proved unattainable. A total of 312 m had been drilled and water struck, but not the much sought-after artesian supply. As demonstrated in the case of Sesami Mission (boreholes B7 and B8), the differences in fluoride content between the two is because B8 is deeper and intersects a potent source of fluoride contamination of which the shallower B7 is spared. Similar situations, backed by a detailed stratigraphic knowledge of the area, can be identified and area-specific borehole depth guidelines formulated.

A somewhat radical but effective method to avoid fluoride poisoning is resettlement. In China, it was recently suggested that 64 000 people in parts of the Shaanxi Province that were worst affected by fluorosis and other endemic diseases be resettled 'because it was cheaper to simply abandon the villages than to bring in safe water and food' (Facker 2001, p.1). A total of 100 000 people in the province had already been disabled by fluorosis and two selenium deficiency diseases, Kashin-Beck and Keshan diseases. In Zimbabwe, a major resettlement drive is currently in progress, but it is mainly aimed at easing population pressure on over-populated communal lands and opening up commercial farming opportunities to those previously disadvantaged in that respect. Future resettlement schemes may consider shifting people from endemic disease-afflicted areas such as Gokwe. The main economic activity in Gokwe is cotton production and if this proposal is to be implemented, agricultural continuity may be ensured by shifting the people to another area conducive to cotton production, if available. If total abandonment is considered a waste of good cotton soils, then farmers can continue utilising their land without necessarily residing on it. The shortest distance from Goredema Clinic (on the very high risk zone) to the no risk zone is only 9 km. Kuwirirana BC in the no-risk zone is only 15 km to the east of Goredema. Planned residential quotas may be developed around Kuwirirana or other places for the farmers. Large paddocks for livestock may be considered in no risk areas.

In Vietnam, UNICEF provided 2000-litre rainwater jars to the fluorosis-prone Khah Hoa District, with remarkable results (*Highlight: clean water* 2000). It is unlikely, however, that the rainwater method can provide adequate supplies throughout the year, unless expensive, well-maintained reservoirs are built. Villagers can also minimize fluoride exposure by desisting from watering vegetables with high-fluoride water. As discussed in Chapter 3, vegetables can take up fluoride from soil and such fluoride can constitute a significant proportion of total dietary fluoride intake. Most artesian boreholes in Gokwe support large vegetable gardens.

7.1.2 Treating Fluoride-rich Water

A number of avenues may be taken to reduce the dissolved fluoride content in drinking water. WHO (2000) categorised water defluoridation methods into sorption, co-precipitation and contact precipitation methods.

7.1.2.1 Sorption methods

In sorption methods, water is filtered through a column packed with a strong adsorbent, such as activated alumina (Al_2O_3) and activated charcoal (e.g. bone charcoal) which takes up fluoride from water (WHO 2000; UNICEF 2002). Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ in bone charcoal is exchanged with fluoride in the following reaction (WHO 2000):

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$$

According to WHO (2000), bone charcoal can be supplied commercially or it can be prepared by heating ground bone to 550° for 4 hours. The general limitations in its use include the production of aesthetically unpleasant water if bone charring is not done correctly, and the taboos associated with the use of animal bones in certain communities (WHO 2000). A requirement that may be laborious is the changing of absorbents when they become saturated with fluoride ions, or backwashing them with a mild acid or alkali solution (WHO 2000; UNICEF 2002).

Brick chips and clay have also been used to pack sorption columns but their defluoridation capacity has been questionable (WHO 2000).

7.1.2.2 Contact Precipitation Methods

The precipitation of CaF_2 from solutions containing Ca, P and F is theoretically feasible, but practically impossible, except in the presence of a catalyst such as bone charcoal (Dahi 1996; WHO 2000). To remove excess fluoride, Ca (e.g. $CaCl_2$) and P (e.g. $NaH_2PO_4.H_2O$, dihydrogenphosphate) compounds are added to water and then the supernatant water is filtered down the bone charcoal column (Dahi 1996; WHO 2000). The reactions involved are as follows (WHO 2000):

- Dissolution of $CaCl_2$

$CaCl_2.\ H_2O\ (s) = Ca^{2+} + 2Cl^- + 2H_2O$

- Dissolution of $NaH_2PO_4.H_2O$

$NaH_2PO_4.H_2O\ (s) = Ca^{2+} + 2Cl^- + 2H_2O$

- Precipitation of CaF_2

$Ca^{2+} + 2F^- = CaF_2\ (s)$

- Precipitation of fluorapatite

$Ca^{2+}\ 6PO_4^{3-}\ + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2\ (s)$

7.1.2.3 Flocculation Methods: The NalgondaTechnique

The Nagonda technique, named after a village in India where it was developed, is aluminium salt-based coagulation-flocculation sedimentation (Dahi et al. 1996; WHO 2000, UNICEF 2002). Alum salt (hydrated aluminium sulphate or aluminium chloride) is dissolved and added to raw water under rapid mixing causing chemical elements to coagulate into aluminium hydroxide micro-flocs that settle to the bottom (WHO 2000; UNICEF 2002). During flocculation, fluoride (and other anions), turbidity, odour, colour, pestsides, organics and some of the bacterial load are removed by electrostastic attachment to flocs, as shown in the following equations (WHO 2000):

- Alum dissolution

$$Al_2(SO_4)_3.18H_2O = 2Al^{3+} 3SO_4^{2-} + 18H_2O$$

- Aluminium precipitation (acidic)

$$2Al^{3+} + 6H_2O = 2Al(OH)_3 + 6H^+$$

- Co-precipitation (none stoichiometric, undefined product)

$$F^- + Al(OH)_3 = \text{Al-F complex} + ?$$

- Adjustment of pH

$$6Ca(OH)_2 + 12H^+ = 6Ca^+ + 12H_2O$$

The pH adjustment, accomplished by the addition of lime, is required to combat acidity of the aluminium sulphate solution and ensure a neutral pH in the treated water.

7.1.2.4 Fluoride Removal Strategies: Applicability to Gokwe

The defluoridation methods described above have been attempted in many parts of the world including Africa (e.g. Tanzania and Kenya), both at household level and on a larger scale, but none of them has been implemented successfully at a large scale (Dahi et al.1996; WHO 2000). High cost (e.g. spare parts and chemicals), the need for skilled operation, and limited efficiency of the methods have been cited as the major drawbacks

It would appear that the Nalgonda method is the most straightforward of the fluoride removal strategies and could be adapted for Gokwe. In Ziurawa village close to Tschoda BC in Gokwe, one household was using alum salt to clear muddy drinking water collected from a shallow well, although there was no excess fluoride in the untreated water (sample w208, 0.19 mg/L F). The addition of alum salt was not accompanied by the addition of lime and consequently the treated water was rather acidic, with a pH of 4.3. It was reported that the use of alum was widespread in the study area, and if this is correct, then many people in Gokwe may already know about the use of alum in water treatment, including fluoride removal. Unfortunately, the chemical is probably being widely used indiscriminately and without the addition of lime. It may be expected that depending on availability of alum (at the time it was widely available on open markets at Gokwe Town) and lime, the Nalgonda technique may be readily acceptable in Gokwe. It would require the construction of sedimentation, filtration and water collection tanks at high fluoride boreholes. In the case of artesian boreholes, infrastructure development will be less demanding as no pumping will be required. At Nembudziya BC, adoption of this method will entail the construction of extra tanks for the process. Currently water from the two boreholes at Nembudziya is first pumped into distribution tanks by a diesel pump from which it is distributed without treatment. In the long run, however, the most cost effective method for Nembudziya is the installation of new boreholes as discussed previously.

7.1.3 Remedial Methods: Concluding Remarks

WHO (2000) suggested that in formulating strategies to counter fluoride poisoning, the provision of alternative low fluoride water sources must be investigated as the first option before considering fluoride removal strategies. In this study, drilling new boreholes less than 2 km from the present locations can solve the fluoride problem at Nembudziya. In other places, such as around Sesami Mission, desisting from sinking boreholes that are unnecessarily deep may solve the problem. Neither of these strategies appears to be applicable on the largest 'very high risk' zone occurrence within the Goredema-Denda-Kahobo area. The former strategy involving the installation of alternative boreholes does not work because the 'no risk' zone lies too far away from the Goredema-Denda-Kahobo area. The latter strategy involving the sinking of boreholes to the correct depth may not work because the area, except where covered by superficial deposits, sits directly upon the Lower Madumabisa Member, one of the formations that contain the potent source of fluoride such that even relatively shallow boreholes are likely to bear fluoride-rich water. Therefore the solution to the fluoride problem in the Goredema-Denda-Kahobo area may lie in some form of resettlement involving partial or total abandonment of the area. Of the fluoride removal strategies, the Nalgonda technique is the most attractive, but may be difficult to implement and maintain under the prevailing socio-economic conditions in the area.

7.2 CONCLUSIONS

Of the dissolved inorganic contaminants determined in waters of the study area, fluoride appears to be the only one that poses a significant health hazard. Sodium, chloride and total dissolved solids (TDS) may be of some concern, but they pose only an aesthetic hazard. Excessive nitrate has been linked to methaemoglobinaemia and cancer but in the study area, the occurrence of nitrate above the health limit is extremely localised, and possibly linked to faecal pollution from pit latrines.

Excessive dissolved fluoride concentrations (F >1.5 mg/L) detected in drinking water from 47 of 196 (24.0%) water sources and from 43 of 94 boreholes (45.7%), portend a major fluorosis risk in the study area. Mathematical interpolation suggests that about 3650 km^2 (60.8%) of the study area sits on ground from which boreholes (existing boreholes or future boreholes) are likely to deliver high fluoride water. Based on the measured and interpolated concentrations of fluoride in water supplies, the study area has been classified into fluorosis-risk zones. The zones, shown on a fluorosis risk map, presage the occurrence of dental fluorosis, skeletal fluorosis and crippling skeletal fluorosis in the study area. In a previous epidemiological survey in part of the current study area, the prevalence of dental fluorosis was found to be 61.9%. Different strategies, including sinking new boreholes in appropriate locations and at optimal depth, and resettlement may be employed to combat the fluoride problem in the area. Defluoridation methods are likely to be unsustainable in the area at present. However, pilot projects on the Nalgonda technique can be considered.

In the central part of the study area, it appears that the fluoride contamination is caused by fluoride-rich water emanating from carbonaceous material (carbonaceous mudstone, carbonaceous shale and sub-bituminous to high-volatile bituminous coal) present in the Lower Madumabisa Member and in the Middle Wankie Member. Such fine-grained materials would normally act as aquicludes, but they can store vast quantities of water and contribute significantly to well yields, particularly where large differential hydraulic heads are encountered. The pervasive E- and NE-trending faults in the area greatly enhance the water-bearing capacity of the shales and mudstones. It has been shown that in general, the greater the thickness of the carbonaceous material traversed by a borehole, the greater the fluoride concentration of the water. The fluoride could be associated with the mineral matter of the carbonaceous material, such as fluorapatite and kaolinite phases.

F concentration generally increases with TDS and NaCl concentrations in the study area, although the highest F concentration range (6-10 mg/L) is not associated with the highest TDS and NaCl concentrations. This suggests a shift in importance of F availability factors in different environments. In hydrogeochemical environments where fluorite is the major F source, F availability via fluorite dissolution could be expected to increase as NaCl concentration increases. The fact that the most fluoriferous waters in the area do not contain the highest TDS and NaCl concentrations suggests that NaCl-controlled fluorite solubility may not be the main F-availability factor in these waters. This can be due to the presence of F sources other than fluorite, such as fluorapatite, kaolinite and trona, whose solubility may not be NaCl-controlled, or due to the increasing influence of other parameters in F availability, such as pH. The association of the highest F concentrations with moderately alkaline conditions suggests that in the most fluoriferous waters of the area, pH-controlled desorption of F from kaolinite supersedes NaCl controlled solubility of fluorite as the main factor in F availability. The release of F adsorbed on kaolinite into groundwater occurs in moderately alkaline (pH 7.8-9) geochemical environments (Hounslow 1995; Ming-Ho 2000).

The known negative correlation between the concentration of calcium and that of dissolved fluoride in natural waters, has not been unequivocally demonstrated in this study. A strong negative correlation, however, exists between the concentrations on Mg and F in waters of the study area.

In some places in the study area, geological structural elements such as faults, have a local influence on the thickness of the fluoride-bearing material that a borehole intersects, thus affecting the intensity of fluoride contamination. Major erosional episodes may also have removed substantial geological materials, including those that are potentially fluoride-bearing, from certain areas.

The granites and gneisses to the east of the study area did not appear to be associated with fluoride contamination of the water. However, elsewhere outside the central part of the study area where Karoo sequences occur, the fluoride distribution is likely to be influenced by the same factors as in the central part.

7.3 FURTHER RESEARCH

This study has focussed on the fluoride content of drinking water, although other parameters of water quality have been included. Some aspects of water quality, notably total alkalinity and trace metal concentrations, have not been considered. An estimate of total alkalinity, can however be obtained from ionic balance calculations involving major ions determined and TDS. The disadvantage of such an indirect method is that any errors in other determinations will be accumulated in the alkalinity data.

Any future water sampling programme for fluoride monitoring in the present study area should focus on boreholes and deeper wells as shallower sources appear to be fluoride-poor. In this study, all boreholes that could be located were visited. However 17 were not sampled because the pumps were in disrepair (Appendix 3). These should be sampled, when functional, to fill the spatial gaps in the database.

Further research can usefully investigate the relationship between fluoride concentration and residence times of water in aquifers. Radiometric dating is probably too expensive to be used for this purpose. Therefore, the use of F, Sr and Li (Edmunds 1994) to estimate residence times might be explored. If, for example, high fluoride concentrations are found to be associated with long residence times, then fluoride distribution can be considered to be related to palaeorecharge, or with recent recharge where fluoride-rich waters have short residence times. Fluoride can be used in conjunction with strontium to characterise aquifers and to identify any mixing between different aquifers (Edmunds 1995; McCaffrey 1998) and thus help identify the fluoride source aquifers.

The determination of the fluoride content of rocks in the study area, particularly of coal and carbonaceous mudstones and shales would prove a useful extension to the present study. Detailed sedimentary and coal petrology and mineralogy will help to establish the fluoride-bearing mineral phases in the aquifers of the study area. Fluoride analysis may also be extended to soils and food crops in the area, including vegetables irrigated with fluoride rich-water. It is also recommended that similar studies in future should consider the analysis of materials suspended in water to assess the role of kaolinite as a fluoride sink.

Studies of the epidemiology of the prevalence and severity of fluorosis in the study area can be better planned with the benefit of results of this study. Aspects of skeletal fluorosis, including radiographic examination of subjects, should be included in the any epidemiological studies. The impact of fluorosis on livestock can also be a subject for further study.

It is also suggested that the Nalgonda Technique of defluoridation be tested in a pilot study in Gokwe District. If successful, it may be implemented more widely in the study area and in other parts of the country affected by fluorosis.

It is clear from the nature of the work proposed here that a multi-disciplinary approach is required to fully understand the causes, effects and extent of fluorosis in the area, and to prescribe suitable remedial measures.

REFERENCES

Adriano, D.C. & Doner, H.E. 1982, 'Bromine, chlorine and fluorine', in A.L. Page (ed), *Methods of Soil Analysis Part 2. Chemical and Microbiological Properties-* Agronomy Monograph no. 9,Part 2 (2^{nd} Edition), Madison Wisconsin, USA, pp. 449-481.

Ait-Kaci Ahmed, A. *(in prep.), The geology of the area north of Gokwe, Gokwe and Kadoma districts*, Zimbabwe Geological Survey Bulletin, no.105, Geological Survey Department, Harare, 85pp.

Alarcón-Herrera, M.T., Martín-Domínguez, I.R.M., Trejo-Vázquez, R. & Rodríguez-Dozal S. 2001, 'Well water fluoride, dental fluorosis, and bone fractures in the Guadiana valley of Mexico', *Fluoride*, vol. 34, no. 2, pp. 139-149.

Andezhath, S.K. & Gosh, G. 1999, Fluorosis management in India: the impact due to networking between health and drinking water supply agencies, *IAHS-AISH* vol. 260, pp.159-165.

Ando, M., Tadano, M., Yamamoto, S., Tamura, K., Asanuma, S., Watanabe, T., Kondo, T., Sakurai S., Ji, R., Liang C., Chen, X., Hong, Z. & Cao, S., 2001, 'Health effects of fluoride pollution caused by coal burning' *Science of the Total Environment*, vol. 271, pp. 107-116. Retrieved: October 6, 2002, from http://www.fluoridealert.org/coal-fluoride.htm

Angmar-Mansson, B. & Whitford, G.M. 1990, 'Environmental and physiological factors affecting dental fluorosis', *Journal of Dental Research*, vol. 69 (Special Issue), pp. 706-713.

Apambire, W.B., Boyle, R.D. & Michael, F.A. 1997, 'Geochemistry, genesis, and health implications of fluoriferous groundwaters in the upper regions of Ghana' *Environmental Geology*, vol. 33, no.1, pp. 13-24.

Bell, F.G., 1998, *Environmental geology*, Blackwell Science, London, 594pp.

Bohmke, F.C & Duncan R.G. 1974, *Final Report on Exploration for Coal and Natural Gas, E.P.O. 378 (Gokwe),* Rio Tinto (Rhodesia) Limited Report [Unpublished].

Bond, G. 1955. 'The Madumabisa (Karoo) shales in the Middle Zambezi Region, *Transactions of the Geological Society of South Africa*, vol. 58, pp. 71-99.

Bouska, V. 1981, *Geochemistry of coal*, Elsevier Publishing Company, New York, 284pp.

Brouwer, I.D.Baker Dirks, O., De Bruin, A. & Hautvast, J.G.A.J. 1988, 'Unsuitability of

World Health Organisation guidelines for fluoride concentrations in drinking water in Senegal, *The Lancet*, vol. 30, pp. 223-235.

Cao, J., Zhao, Y., Liu, J., Xirao, R., Danzeng. S. 2000, 'Flouride concentration of water sources in Tibet', *Fluoride*, vol. 33, no. 4, pp. 205-209.

Carnow, B.W. & Conibear, S.A. 1981, 'Industrial Fluorosis', *Fluoride* vol. 14, no.14, pp 172-181. Retrieved: October 6, 2002, from http://www.fluoridealert.org/i-flurosis.htm

Carton, R.J. 1991, 'Comments on reevaluating the fluoride in drinking water standard'. Retrieved: August 26, 2002, from http://www.rvi.net/~fluride/carton.htm

Cauley J.A., Murphy P.A., Riley P.J. & Buharit A.M. 1995, 'Effects of fluoridated drinking water on bone mass and fractures: the study of osteoporotic fractures, *Journal of Bone and Mineral Research*, vol. 10, no. 7, pp. 1076-1086.

Cerklewski, F.L. 1997, 'Fluoride bioavailability-nutritional and clinical aspects', *NutritionResearch*, vol. 17, no.5, pp. 907-929, Elsevier Science, Washington D.C.

Chen M.J. 1991, *An investigation of endemic fluorine poisoning caused by food contaminated by smoke containing fluoride*'. Retrieved: October 6, 2002, from http://www.fluoridealert.org/coal-fluoride.htm

Choubisa, S.L. 1998. 'Fluorosis in some tribal villages of Udaipur district (Rajasthan)', *Journal of Environmental Biology* vol. 19, no. 4, pp.341-352. Retrieved: April 27, 2001, from GEOBASE database.

CSIR (Centre for Scientific and Industrial Research) 1991, *Reccommendations to the Department of water affairs, Bophuthatswana on criteria for drinking water quality,* Internal Report no. 10/8/4/3/32508, CSIR, Pretoria, 9pp.

Dahi, E., Mtalo, F., Njau B.,Bregnhj, H 1996, 'Defluoridation using the Nalgonda technique in Tanzania', *Reaching The Unreached: Challenges of the 21st Century,* 22nd WEDC Conference, New Delhi, India.

Dahi, E. 1996, 'Contact precipitation for defluoridationof water', R*eaching The Unreached: Challenges of the 21st Century,* 22nd WEDC Conference, New Delhi, India.

Danielson, C., Lyon, J.L., Eager, M, Goodenough, G.K. 1992, 'Hip fractures and fluoridation in Utah's elderly population', *JAMA,* vol. 265, pp.746-748.

Davies, S.N. & DeWiest, J.M. 1966, *Hydrogeology,* John Wiley & Sons, Sydney, 463pp.

Day, F.H. 1963, *The chemical elements in nature,* George Harrap & Co, London, 372pp.

Dean, H.T. 1934, 'Classification of mottled enamel diagnosis', *Journal of American Dental Association*, vol. 21, pp. 1421-1426.

Dean, H.T. 1942, 'The investigation of physiological effects by the epidemiological method', in F.R. Moulton (ed), *Fluorine and dental health*, American Association for the Advancement of Science, publication no. 19.

Den Besten, P.K. & Crenshaw 1987, 'Studies on the changes in developing enamel caused by ingestion of high levels of fluoride in the rate', *Advances in Dental Research*, vol.1, pp. 176-180.

DEP (Department of Environmental Protection) 2001, 'Drinking water inorganic contaminants', DEP, Florida, USA. Retrieved: April 4, 2002, from http://www.dep.state.fl.us/water/drinkingwater/inorg_con.htm

Dissanayake, C.B. 1996, 'Water quality and dental health in the dry zone of Sri Lanka', in J.D. Appleton, R. Fuge & G.J.H. McCall (eds.), *Environmental geochemistry and health*, Geological Society Special Publication, no.13, pp. 131-140.

Edmunds, W.M. 1995 'Characterisation of groundwaters in semi-arid and arid zones using minor and major elements', in H. Nash & G.J.H. McCall (eds), *Groundwater quality*, Chapman & Hall, London, pp. 19-30.

Edmunds, W.M. & Smedley 1996, 'Groundwater geochemistry and health: an overview', in J.D. Appleton, R. Fuge & G.J.H. McCall (eds.), *Environmental geochemistry and health*, Geological Society Special Publication, no.13, pp. 91-105.

ESRI™ (Environmental Systems Research Institute, Inc.) 1996, *ArcView Spatial Analyst*, ESRI™, USA, 147pp.

Facker, M. 2001, ' China to relocate 64 000 villagers from areas plagued by chronic heart, bone diseases', Associated Press, December 12, 2001. Retrieved: October 6, 2002, from http://www.fluoridealert.org/news/china-india.htm

Fejerskov, O., Yanagisawa, T., Tohda, H. Larsen, M.J. & Josephsene, K. 1991, 'Posteruptive changes in human dental fluorosis- a histological and ultrastructural study, *Proceedings of the Finnish Dental Society*, vol. 87, pp. 607-619.

Fluoride (n.d.) Retrieved: February 16, 2003, from http://www.who.int/docstore/water_sanitation_health/GDWQ/draftchemicals/fluoride2003.pdf+chapter8

Fluoride measurement: in recent years public awareness of drinking water. Retrieved: April 4, 2002, from http://www.chem.ubc.ca/courseware/211/F.pdf

Gaciri, S.J. & Davies, T.C. 1993, 'The occurrence and geochemistry of fluoride in some natural waters in Kenya', *Journal of Hydrology,* vol 143, pp. 395-412.

Galagan, D. 1953, 'Climate and controlled fluoridation', *Journal of the American Dental Association,* vol. 47, pp. 159-170.

Garande, J. 1990, 'A preliminary report on boreholes drilled for water along the Gokwe-Siabuwa road, north-west of Gokwe', *Annal of Zimbabwe Geological Survey,* vol. XIV, pp. 64-67.

Gedalia, I. & Shapira, L. 1989, 'Effect of prenatal and postnatal fluoride on the human deciduous and dentition. A literature review', *Advances in dental research,* vol. 3, pp. 168-176.

Global Literature Life 1990, *Global Life Literature Boreholes 1732 (Mutewe)*, GLL Report [Unpublished].

Goldschmidt, V.M. 1962, *Geochemistry,* Oxford, Great Britain, 730pp.

Guo, M.K., Nopakun, J., Messer, H.H., Ophaung R. & Singer, L. 1988, 'Retention of skeletal fluoride during bone turnover in rats, *Journal of Nutrition,* vol.118, pp. 362-366.

Harshan, K.D. 1995, *Water sampling for pollution monitoring*, Godorn and Beach Publishers, London.

Hem, J.D. 1985, *Study and interpretation of the chemical characteristics of natural water,* US Geological Survey Water-Supply Paper, no. 2254

Highlight: clean water 2000. Retreived: September 03, 2002, from http://www.unicef.org.vn/fluoridize.htm

Hillier, S., Cooper, C., Kellingray, S., Russel, G., Hughes, H., Coggon, D. 2000, 'Fluoride in drinking water and the risk of hip fracture in the UK: a case control study' *The Lancelot*, vol. 355, pp. 265-269, University of Southampton, UK.

Hodgson, J.F., Allaway, W.H. & Lockman R.B. 1971, 'Regional plant chemistry as a reflection of the environment', in H.L. Cannon & C.H. Howard (eds), *Environmental geochemistry in health and disease*, Geological Society of America Inc., Colorado, pp. 57-72.

Hounslow, A.W. 1995, '*Water quality data: analysis and interpretation*', CRS Press, Inc.,New York, USA.

INTERCONSULT^{AS} 1985. 'Hydrogeology'. *National Master Plan for Rural Water Supply and Sanitation,* Annex 1 to Volume 2^2, 64pp.

The University of Adelaide, (n.d.). Retrieved: March 04, 2002, from http://www.chemistry.adelaide.edu/external/Soc-Rel/Content/ise.html

Jenkins, G.N. 1990, 'The metabolism and effects of fluoride', in N.D.Priest; & F.L. Van De Vywer (eds), *Trace metals and fluoride in bones and teeth,* CRC Press, Boca Raton, pp. 142-173.

Jones, C.M. & Worthington, H. 2000. 'Water fluoridation, poverty and tooth decay in 12-year-old children', *Journal of Dentistry,* vol. 28, pp. 389-393.

Koniekzka, P , Zygmunt, B., Namisnik, J. 2000, 'Comparison of fluoride ion-selective potentiometric methods of fluoride determination in human urine', *Bulletin of Environmental Contamination and Toxicology,* vol. 64, pp. 794-803.

Koritnig, S. 1978. 'Flourine', in K.H. Wedepohl (executive editor) and C.W. Correns, D.M. Shaw, K.K. Turekian & J. Zemann (eds), *Handbook of geochemistry,* vol. II/1, pp. 9-C-1 to 9-O-3, Springer Verlag, Berlin.

Larsen, M.J., Richards, A, & Fejerskov, O. 1985 Development of dental fluorosis according to age at the start of fluoride administration, *Carries Research,* vol. 19, pp. 519-527.

Lepper, J 1992, *The Lower Karoo in the Mid-Zambezi Basin (Zimbabwe),* Geologishes Jabhrbuch, Hannover, 38pp.

Leyshon, P.R. 1969, *The geology of the country around the Copper Queen*, Rhodesia Geological Survey Bulletin, no. 66, Geological Survey Department, Salisbury 147pp.

Lister, L.A. 1987, *Erosion Surfaces of Zimbabwe,* Zimbabwe Geological Survey Bulletin, no. 95, Geological Survey Department, Harare.

Mabelya, L., Helderman, W.H.V., Vanthof, M.A., Konig, K.G. 1997, 'Dental Fluorosis and the use of a high fluoride-containing trona tenderiser (Magadi)', *Community Dentistry and Oral Epidemiology,* vol. 25, no. 2, pp. 170-176.

Madans, J., Kleinman, J.C. & Ccoroni-Huntley J 1983, 'The relationship between hip fracture and water fluoridation: an analysis of national data', *American Journal of Public Health,* vol. 73, pp. 296-298.

Magalela, W. 1997. 'Some aspects of saline groundwaters in the Gokwe District', *Annals of the Zimbabwe Geological Survey,* vol. XVIII, pp. 32-36.

Mann, J., Mahmoud, W., Ernest, M., Sgan-Cohen, H., Shoshan, N. & Gedalia, I. 1990, 'Fluorosis and carries in 6-8 year-old children in a 5 ppm fluoride area', *Community Dentistry and Oral Epidemiology,* vol. 18, pp. 77-79.

Martin, B. 1991. *Scientific knowledge in controversy: The social dynamics of the fluoridation debate,* State University of New York, USA, 266pp.

Maynard, J.B. 1991. 'Shale hosted deposits of Pb, Zn, and Ba: syngenetic deposition from exhaled brines in deep marine basins', in E.R. Force, J.J. Eidel and J.B. Maynard (eds) Sedimentary and diagenetic mineral deposits: a basin analysis approach to exploration, *Reviews in economic geology*, vol. 5, pp.177- 1185.

McCaffrey, L.P. 1998, 'Distribution and causes of high fluoride groundwater in the western Bushveld area of South Africa', *PhD Thesis,* University of Cape Town, South Africa [Unpublished].

McCoy, J. & Johnston K. 2001, *Using ArcGIS™ Spatial Analyst,* ESRI™, USA, 230pp.

Method 9214: Potentiometric determination of fluoride in aqueous samples with ion selective electrode 1996. Retrieved: March 03, 2002, from http://www.epa.gov.epaunswer/hazwaste/test/9214.pdf

Mills, C.F. 1996, 'Geochemical aspects of the aetiology of trace element related diseases, in J.D. Appleton, R. Fuge, G.J.H. McCall (eds.), *Environmental geochemistry and health,* Geological Society Special Publication, no.13, pp. 1-5.

Ming-Ho, Y. 2000, *Environmental toxicology: impacts of environmental toxicants on living systems,* CRC, Florida, USA, 255pp.

Moller, I.J. 1982, 'Fluoride and dental fluorosis', *International Dental Journal,* vol. 32, pp. 135-147.

Moynahan E.J. 1980, 'Trace elements and man', *Environmental geochemistry and health,* Royal society of London, pp. 65-79.

NRC (US National Research Council) 1993, *Health Effects of Ingested Fluoride,* National Academy Press, Washington, 181pp.

Owen, P., F.B. Jones 1995, 'Main factors affecting the composition of natural waters', in B. Salbu & E. Steinnes (eds), *Trace elements in natural waters,* p1-20, CRC Press, Tokyo.

Plant, J. Baldock J., Haslam H., & Smith B. 1998, 'The role of geochemistry in environmental and epidemiological studies in developing countries: a review, in J.D. Appleton, R. Fuge & G.J.H. McCall (eds.), *Environmental geochemistry and health,* Geological Society Special Publication, no.13, pp. 7-22.

Price, M. 2000, *Introducing groundwater,* Chapman & Hall, London, 278pp.

Report on prospecting operations in eastern Sebungwe, exclusive prospecting reservation no. 14, 1951, Zimbabwe Geological Report [Unpublished].

Richards, A.,Fejerskov O., Baelum, V. 1989, 'Enamel fluoride in relation to severity of human dental fluorosis', *Advances in Dental Research,* vol. 3, pp. 147-153.

Riggs, R.L., Hodgson, S.F., O'Fallon, W.M., Chao, E.Y.S., Wahner, H.W., Muhs, J.M., Cedel, S.L. & Melton, L.J. 1990, 'Effect of fluoride treatment on the fracture rate in postmenoposal women with osteoporosis, *New England Journal of Medicine,* vol. 322, pp. 802-809.

Riley, J.C., Lennon M.A., Ellwood R.P. 1999, 'The effect of water fluoridation and social inequalities on dental carries in 5-year old children', *International Journal of Epidemiology,* vol.28, issue 2, pp.300-305.

Rundle, C. C. 2000. *A beginners guide to ion-selective electrode measurements,* Retrieved: February 10, 2002, from http://www.nico2000.net/Book/

Schultz, H., Hattman, E.A. & Booher W.B. 1973. 'The fate of some trace elements during coal pre-treatment and combustion', in P.S. Babu (ed), Trace elements in fuel, *Advances in Chemistry Series* vol. 141, pp.139-153, American Chemical Society, USA

Sinha, S., Saxena R., Sighn, S. 2000, 'Fluoride removal from water by *Hydrilla verticata* (I.f.) Royle and its toxic effects', *Bulletin of Environmental Toxicology,* vol. 65, Springer- Verlag, New York, pp. 683-690.

Smith, F.A. & Hodge, H.C. 1979, 'Airborne fluorides and man', *Critical Reviews of Environmental Control,* vol. 9, pp. 1-25.

Spencer, H., Osis, D., Kramer, L., Wiatrowski, E., Norris, C. 1975, 'Effect of calcium and phosphorus on fluoride metabolism in man', *Journal of Nutrition,* vol. 105, pp. 733-740.

Spencer, H., Kramer, L., Wiatrowski, E., Osis, D. 1978, 'Magnesium-fluoride interrelationships in man. II. Effect of magnesium on fluoride metabolism, *American Journal of Physiology,* vol. 234, pp. E343-E347.

Speight, G.J 1994, *The chemistry and technology of coal,* Marcel Dekker, Inc., New York, 641pp.

Sowers, M.F.R., Clark, M.K., Jannausch, M.L. & Wallace, R.B. 1991, 'A prospective study of bone mineral content and fracture in communities with differential fluoride exposure', *American Journal of epidemiology,* vol 133, no. 7, pp. 649-660.

Suckling, G., Thurnley, D.C. & Nelson D.G.A. 1988, 'The macroscopic and scanning electron-microscope appearance and microhardness of the enamel, and the related histological changes in the enamel , and the related histological changes in the enamel organ of erupting sheep incisors resulting from prolonged low daily dose of fluoride', *Journal of Dairy Science,* vol. 55, pp. 790-804.

Sutton, E.R. 1979, *The geology of the Mafungabusi area*, Rhodesia Geological Survey Bulletin, no. 81, Geological Survey Department, Salisbury, 318 pp.

Thylstrup, A. 1978, 'Distribution of dental fluorosis in the primary dentition', *Community Dentistry and Oral Epidemiology*, vol 6, pp. 329-337.

Thylstrup A., 1983, 'Posteruptive development of isolated and confluent pits in fluorosed enamel in a 6-year-old girl', *Scandinavia Journal of Dental Research,* vol. 91, pp. 243-246.

Thompson, A.O. 1981, *The geology of the Lubimbi, Dahlia and Hankano coalfields, Wankie and Lupane districts,* Zimbabwe Geological Survey Bulletin, no 88, 88pp.

Tobayiwa, C., Musiyambiri, M., Chironga, I., Mazorodze, O. & Sapahla, S. 1991, 'Fluoride levels in two districts in Zimbabwe', *Central African Journal of Medicine,* vol. 37, no.11, pp. 353-361.

Underwood, E.J. 1980, 'Trace elements and health: an overview', *Environmental Geochemistry and Health,* Royal Society of London, pp. 5-14.

UNICEF (United Nations International Children and Education Fund) 2002. *Fluoride in water: An overview,* Retrieved: October 06, 2002, from: http://www.unicef.org/programme/wes/info/fluor.htm

EPA (US Environmental Protection Agency) 1985, *Drinking water criteria document on fluoride,* Office of Drinking Water, EPA, Washington D.C., TR-832-51985.

Vinogradov, A.P. 1959, *The geochemistry of rare and dispersed chemical elements in soils,* Chapman and Hall, London, 209pp.

Wang, X.C., Kawahara, K. & Guo, X.J. 1999, 'Fluoride contamination of groundwater and its impacts on human health in Inner Mongolia area' *Aqua,* vol. 48, no. 4, pp. 146-153. Retrieved: April 27, 2001, from GEOBASE database.

Warnakulasuriya, K.A.A.S., Balasuriya, S. Perera, P.A. & Peiris, L.C 1992, 'Determining optimal levels of fluoride in drinking water for hot dry climates- a case study in Sri Lanka, *Community Dental and Oral Epidemiology,* vol. 20, pp. 125-128.

Whitford, G.M. 1989, 'The metabolism and toxicity of fluoride', in H.M. Myers (ed)

Monographs in Oral Science, no.13.

Whitford, G.M. & Pashley D.H. 1991, 'Fluoride reabsorption by non-ionic diffusion in the distal nephron of the dog, *Proceeding of the Society of Experimental Biological Medicine,* vol. 196, pp. 178-183.

WHO (World Health Organisation) 1984, 'Guidelines for drinking water quality', vol. 1 (Recommendations), Geneva, 130pp.

WHO (World Health Organisation) 1993, 'Guidelines for drinking-water quality, second edition', vol. 1 (Recommendations), WHO, Geneva.

WHO (World Health Organisation) 1996, 'Guidelines for drinking-water quality, second edition', vol. 2 (Health criteria and other supporting information), WHO, Geneva, pp. 231-237.

WHO (World Health Organisation) 2000, *Fluoride in drinking water*- Draft II. Retrieved: August 26, 2002, from http://www.who.int/environmental_information/Information_resources/htmdocs/Fluoride/fluoride.html

Where we need to act 2001, 'Water for health-taking charge', World Water Day 2001 Report, Chapter 3, Retrieved: September 3, 2002, from http://www.worldwaterday.org/2001/report/ch3.html

Zellmer, D.L. 1999, *The fluoride ion selective electrode experiment: Direct potentiometry and standard addition methods.* Retrieved: March 03, 2002, from http://crstal.biol.csufresno.edu:8080/davidz/Chem102/FluorideISE/FluorideISE.html

Zietsman, S. 1989, 'The relationship between the geological variation, the F-content of the water and the spatial variation in the occurrence of dental fluorosis in an endemic area', *South African Geographical Journal,* vol.71, no.2, pp. 102-108

ZINWA (Zimbabwe National Water Authority). *Borehole Data for Gokwe District.* [Unpublished File].

APPENDICES

Appendix 1: Water Sample Attributes

Attributes of water samples variously referred to in this thesis are put together in this appendix. The primary key or common point of reference in this appendix is the unique Sample ID. The numbers in brackets next to some sample IDs indicate the number of instances water from the corresponding source was re-sampled and analysed by the fluoride ion selective electrode (FISE) in the field. The corresponding F⁻ (E) value (fluoride concentration measured by FISE) represents an average fluoride concentration from the instances of FISE measurement. The rest of the FISE results are single-instance measurements. F⁻ (C) represents fluoride concentration as determined by High Performance Ion Chromatography (HPIC). The eastings and northings are based on the Universal Transverse Mercator (UTM) grid (Zone 35). Altitude is given in metres above mean sea level and SWL (static water level) refers to the depth from ground level to the water surface in a water source. In the appendix, Ec stands for electrical conductivity and TDS total dissolved solids. Blank cells indicate that the corresponding parameters were not measured.

The water sources are artesian boreholes (ARTES), pumped boreholes (BHOLE), deep wells (DWELL), shallow wells (SWELL), riverbed sediment wells (RBSED), flowing streams (FSTRM), stagnant streams (SSTRM), springs (SPRNG) and dams (DAMWA).

Water Sample ID	Water Source	Easting (UTM)	Northing (UTM)	Altitude (m)	SWL (m)	Ionic concentrations in mg/L									Temp (°C)	pH	E/C mS/cm	TDS (ppm)
						F⁻(E)	F⁻(C)	Cl⁻	NO_3^-	SO_4^{2-}	Na⁺	K⁺	Mg	Ca²⁺				
w004 (2)	BHOLE	0702407	8025377	863	12	7.76	7.60	102.21	0.19	298.40	39.82	0.33	0.39	0.11	26.80	8.20	1.50	748
w005 (2)	ARTES	0697274	8023933	[illegible]		8.94	11.03	32.19	1.27	298.40	318.40	3.06	2.07	4.29	29.30	8.20	1.34	663
w006	BHOLE	0694650	8023121	832		8.52	8.10	29.25	0.83	102.50	311.21	3.12	2.06	4.04	29.10	8.30	1.50	688
w007	RBSED	0690240	8020615	836	2	0.18									26.60	6.10	1.38	77.7
w008 (3)	BHOLE	0682946	8014669	836		[illegible]									36.60	8.40	1.01	504
w012 (2)	ARTES	[illegible]	8018189	788		5.29	5.61	11.87	0.00	130.30	712.20	98.04	134.37	151.15	36.50	8.40	1.32	658
w013 (3)	BHOLE	[illegible]	[illegible]	744		1.08	1.07	0.60	7.97	119.16	402.78	1.56	10.85	7.19	27.50	7.20	1.57	790
w014 (2)	BHOLE	[illegible]	[illegible]	820		0.05	0.18	6.10	1.62	6.79	20.62	2.00	0.13	0.29	28.50	5.70	0.12	118
w015 (2)	SWELL	0661597	8048146	764	2	0.06									24.60	6.00	0.56	43
w017 (2)	BHOLE	0701144	8025535	852	18	7.55	8.30	22.20	0.00	73.23	299.25	3.47	2.49	5.60	26.70	8.20	1.60	802

Water Sample ID	Water Source	Easting (UTM)	Northing (UTM)	Altitude (m)	SWL (m)	Ionic concentrations in mg/L F (E)	F (C)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Temp (°C)	pH	E/C mS/cm	TDS (ppm)
w018 (2)	BHOLE	0706902	[illegible]	916	34	5.49	4.83	21.96	0.00	94.78	225.91	5.21	6.28	11.21	26.60	7.80	1.59	[illegible]
w019	BHOLE	0713571	8020439	787		0.08									28.40	6.60	1.17	[illegible]
w020	BHOLE	0714965	8019354	998		0.12	0.00	11.71	10.94	0.70	23.73	1.23	19.25	33.54	26.90	7.00	1.01	[illegible]
w021	BHOLE	0713563	8020447	987		0.07	0.00	74.35	11.50	0.57	34.75	1.50	42.15	17.55	26.60	6.60	1.12	560
w022	SWELL	0704440	8027908	881	2	0.04	0.04	3.84	2.41	0.80	15.37	1.01	0.60	2.30	17.20	6.20	0.08	44.6
w023	SWELL	0704370	8027964	880	1.5	0.14	0.08	3.29	0.93	23.51	17.34	0.60	0.29	1.41	18.90	5.00	0.09	46.6
w024	SWELL	0709392	8021835	958	1.5	0.80	0.00	4.30	5.73	219.12	57.98	1.32	16.96	121.53	19.30	7.20	1.23	616
w025	BHOLE	0707041	8017782	934		0.27	0.14	0.36	30.86	1.38	44.06	2.73	40.39	14.34	28.00	6.90	0.85	423
w026 (2)	BHOLE	0705685	8019598	911	33	7.00	5.03	14.11	0.00	[illegible]	111.43	3.21	4.02	7.07	28.60	7.90	1.21	[illegible]
w027	RBSED	0705829	8018948	914	4	0.29	0.00	5.06	9.41	86.12	14.61	5.27	114.38	34.42	21.70	7.30	1.38	690
w028	SWELL	0705871	8018881	915	2.5	0.43	0.39	2.38	3.91	127.93	16.10	1.80	57.37	39.35	24.80	7.30	1.02	[illegible]
w029 (2)	ARTES	0698421	8027272	825		6.65	6.05	28.41	0.00	50.61	[illegible]	4.16	2.67	0.48	25.50	8.00	1.59	[illegible]
w030 (2)	BHOLE	0696601	8028827	817		4.86	8.30				305.00	5.41	5.24	11.36	26.90	7.20	2.52	[illegible]
w031	RBSED	0696556	[illegible]	817	5	0.15									19.70	6.90	0.92	[illegible]
w032	RBSED	0696017	8021020	846	4	0.14	0.00	6.41	0.00	[illegible]	63.08	14.57	88.69	70.14	21.70	6.80	1.95	970
w033	RBSED	0700067	[illegible]	817	4.5	0.65	0.42	4.32	1.49	157.25	34.61	3.17	48.88	23.23	19.30	7.00	1.22	610
w034	RBSED	0700702	[illegible]	850	6	0.88	0.58	8.85	0.00	[illegible]	34.92	14.36	56.52	188.70	16.20	7.50	1.93	960
w035	RBSED	0701212	8025026	855	5	0.56	0.71	4.02	1.49	632.45	61.27	19.66	32.28	121.53	19.10	7.50	1.54	770
w036	BHOLE	0706123	[illegible]	[illegible]		5.68	2.66	29.90	0.00	269.89	327.57	4.47	8.83	15.62	28.60	7.50	2.25	1121
w037	RBSED	0690258	8020620	[illegible]	4.5	0.30	0.24	10.40	0.23	2.96	47.36	8.98	5.98	7.43	22.40	6.20	0.40	204
w041 (3)	ARTES	0680241	8016257	802		4.94	4.66	14.07	0.00	138.26	152.07	2.21	0.84	1.93	36.20	8.30	1.19	[illegible]
w042	BHOLE	0677478	8022492	765		3.50	2.11	11.20	1.96	131.81	317.48	1.49	11.34	11.83	27.60		1.97	[illegible]
w043 (2)	ARTES	0674714	8025414	770		8.00	7.20	74.67	0.00	[illegible]	359.65	5.79	1.52	5.37	34.10	7.40	2.28	1140
w044 (2)	ARTES	0670278	8025664	750		5.73	5.70	290.98	41.83	[illegible]	639.86	7.74	3.81	15.89	35.10	7.10	5.43	2680
w045 (2)	ARTES	0682727	8015557	804		4.45	3.25	5.05	0.00	1.02	90.03	1.00	0.47	1.30	28.40	7.90	1.11	550
w046	BHOLE	0672159	8030984	742	7.5	0.37	0.66	9.41	0.00	8.23	[illegible]	14.05	9.26	7.58	25.70	7.50	0.80	400
w048	BHOLE	0671509	8031710	740	8	0.36	0.00	4.65	0.00	48.14	68.60	2.33	15.08	8.87	27.40	6.90	1.05	520
w050	ARTES	0669080	8032829	738		5.31	4.31	377.33	0.00	1.02	450.91	7.29	[illegible]	7.95	31.30	7.20	4.58	2280
w051 (2)	ARTES	0667068	8036049	730		4.14	3.92	370.98	0.00	1.71	[illegible]	3.97	2.36	8.58	[illegible]	7.50	5.97	2980
w052	DWELL	0667164	8036066	730	7.5	0.11	0.00	4.09	0.00	157.45	95.98	4.79	24.98	49.22	[illegible]	6.80	1.23	610
w053	SSTRM	[illegible]	[illegible]	728	3	0.24	0.20	3.91	0.04	16.16	69.56	3.80	16.77	23.09	25.50	7.20	0.63	310
w055 (2)	ARTES	0660902	[illegible]	660		4.48	4.10	6.99	1.62	6.79	796.00	14.35	5.92	34.24	33.30	6.90	0.38	[illegible]
w056	RBSED	0660851	[illegible]	660	4	0.79	0.75	315.75	1.39	8.83	794.11	10.76	11.60	27.69	23.10	7.20	6.90	[illegible]

Water Sample ID	Water Source	Easting (UTM)	Northing (UTM)	Altitude (m)	SWL (m)	Ionic concentrations in mg/L									Temp (°C)	pH	E/C mS/cm	TDS (ppm)
						F⁻(E)	F⁻(C)	Cl⁻	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}				
w059 (2)	ARTES	0666247	8056576	673		4.76	4.37	607.69	0.00	2.35	478.35	5.17	3.04	12.07	31.90	7.00	6.42	3210
w060	BHOLE	0670749	8059338	668	10	0.32	0.08	2.79	2.00	33.82	77.48	5.47	19.60	20.59	25.80	6.80	1.05	520
w061 (3)	BHOLE	0712624	8039503	889	44	3.19	2.68	38.19	3.01	189.95	298.16	4.85	4.69	5.97	24.00	7.20	1.67	830
w062 (2)	BHOLE	0714140	8044803	866		2.80	2.85	34.79	2.63	191.18	339.64	6.23	5.47	12.57	27.00	7.50	1.42	740
w063	RBSED	0664297	8035152	727	1.5	0.25					20.01	28.91	6.66	15.89	23.50	7.60	0.39	195.1
w064	FSTRM	0655222	8031211	802		0.19	0.12	59.88	0.00	0.54	75.18	15.36	3.99	6.13	21.60		0.45	229
w065	SPRNG	0655085	8031151	805		0.10	0.05	19.44	11.77	2.11	31.75	15.13	4.02	7.91	21.70	6.20	0.26	133
w066	DWELL	0657957	8031223	806	11	0.16	0.32	20.64	76.08	17.16	71.08	17.29	6.31	10.31	25.30	6.40	0.37	180
w067	DWELL	0657331	8030612	824	3.5	0.06	0.13	19.95	6.54	10.60	18.33	10.61	3.32	9.47	22.60	6.30	0.24	1.2
w068	BHOLE	0657306	8030598	824	3.5	0.08	0.06	10.99	0.00	1.45	14.12	10.28	3.31	9.84	24.80	6.80	0.18	90.6
w069	DWELL	0657185	8030506	827	4.5	0.00	0.10	14.67	34.71	4.99	9.64	13.02	3.90	14.90	24.10	5.70	0.20	100
w070	BHOLE	0648259	8009563	926	49	0.07					29.22	7.77	2.67	5.07	27.70	6.10	0.19	95.5
w071	SWELL	0655692	8020059	860	1	0.04	0.17	0.16	51.39	5.73	21.34	13.39	5.23	12.21	22.00	5.50	0.17	86.5
w072	SWELL	0658952	8022124	830	1.5	0.00	0.14	2.64	25.48	1.58	41.32	27.09	2.93	1.53	23.30	5.10	0.12	64.9
w075	SWELL	0666507	8028112	769	3	0.00					9.59	5.54	0.38	0.30	21.70	5.20	0.06	34.5
w076	SWELL	0667702	8029875	754	3	0.21					9.61	30.51	0.94	0.94	24.70	5.50	0.06	31.8
w078	SWELL	0680467	8011410	834	2	0.08	0.20	2.68	2.35	6.03	5.97	1.99	0.52	0.98	19.10	5.10	0.06	35.5
w079	BHOLE	0679305	8010554	841	13	4.29									25.80	7.70	1.76	876
w080	SWELL	0679541	8010211	842	3.4	0.31	0.00	23.81	109.11	82.41	117.76	20.78	32.37	5.03	25.20	7.20	1.15	576
w081	SWELL	0679593	8010167	842	2.5	0.15	0.24	11.67	39.88	3.79	11.00	12.10	1.88	1.05	21.60	5.20	0.23	116
w082	RBSED	0678563	8009407	848	3	0.34					69.78	12.72	45.06	15.66	23.50	6.50	0.75	378
w083	SWELL	0679822	8010659	839	2	0.56					17.05	3.68	0.63	0.53	23.30	6.50	0.06	30.5
w085	ARTES	0682459	8014238	822		8.38									26.10	7.60	2.16	1091
w086	RBSED	0694076	8023246	830	1	0.28					23.12	24.00	77.91	14.76	21.60	6.80	1.23	614
w087	RBSED	0700965	8013144	904	1	0.23	0.50	34.52	0.00	663.41	118.56	9.27	87.03	71.78	21.70	7.10	1.31	650
w088	SSTRM	0701323	8012890	905		0.42	0.37	11.36	0.00	272.21	99.17	20.16	62.88	71.45	22.90	7.90	1.64	816
w089	SSTRM	0701349	8012606	906		0.19	0.17	0.12	6.40	14.61	29.87	4.15	20.13	10.53	23.30	8.00	0.53	264
w092	FSTRM	0693341	8030504	803	4	0.74	0.40	6.42	0.00	117.98	89.07	5.82	33.38	12.30	19.50	8.30	1.09	546
w093 (2)	ARTES	0693034	8032444	796		7.26	4.17	5.32	0.00	137.33	[illegible]	2.65	1.22	5.47	33.60	7.80	1.99	991
w094	RBSED	0690232	8033666	780	2	0.61	0.13	6.80	0.63	0.57	110.38	8.25	39.59	54.99	23.30	7.00	1.01	513
w095	RBSED	0690313	8033533	781		0.71	0.60	3.82	4.76	294.94	68.96	12.31	29.52	20.37	25.20	7.00	0.93	464
w096 (2)	BHOLE	0687124	8038058	751		6.20	5.95	111.19	0.00	0.19	210.23	4.49	3.01	4.37	21.60	8.60	2.60	1297
w09[illegible]	ARTES	0684524	8030102	772		4.12	6.68	96.44	1.35	1199.60	[illegible]	3.82	2.37	7.48	32.00	8.10	2.51	1243

Water Sample ID	Water Source	Easting (UTM)	Northing (UTM)	Altitude (m)	SWL (m)	Ionic concentrations in mg/L									Temp (°C)	pH	E/C mS/cm	TDS (ppm)
						F⁻(E)	F⁻(C)	Cl⁻	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}				
w098	SWELL	0685352	8043158	742	3.5	0.20									25.00	7.20	0.99	494
w099	DWELL	0685340	8043257	742	3.5	0.54	0.19	0.28	0.15	21.79	95.59	0.78	17.83	8.40	26.50	7.30	0.80	402
w100	FSTRM	0680781	8052860	701		0.66	0.48	[illegible]	0.43	504.82	288.18	17.33	41.34	8.35	23.80		1.45	720
w101 (2)	BHOLE	0675466	8053879	693		5.64	5.53	[illegible]	0.00	4.53	545.74	11.30	4.38	7.55	32.30	7.80	4.19	2100
w102	SWELL	0666565	8057600	666	0.5	0.52	0.59	16.39	1.53	20.11	105.60	22.97	15.77	5.51	23.90	7.90	0.52	264
w103 (2)	BHOLE	0659689	8050575	693	13	0.33	0.27	10.76	0.09	15.43	40.19	2.22	8.24	5.22	26.20	7.60	0.57	[illegible]
w104	ARTES	0658752	8049792	714		2.69	3.03	1224.32	244.86	0.00	210.93	5.38	2.81	4.65	37.30		5.89	[illegible]
w105	BHOLE	0649148	8051045	652		3.13									28.60	7.30	5.74	2870
w106	DWELL	0667164	8036173	730		0.19	0.00	2.34	0.42	42.26	35.80	4.09	20.92	13.50	25.00	7.90	0.80	407
w107 (2)	BHOLE	0683834	8014196	826	15	0.66	0.65	16.76	0.66	30.27	92.02	3.17	0.84	13.17	23.70	7.70	0.84	418
w108 (2)	ARTES	0683820	8014309	826		2.87	3.43	15.18	0.67	120.28	197.26	2.34	2.54	4.04	22.00	8.50	0.85	427
w109	BHOLE	0711858	8021953	960	31	0.13									28.70	6.90	0.94	469
w110	DAMWA	0714427	8045370	864		0.19									18.90	6.60	0.14	71
w112	BHOLE	0711007	8054097	846		0.51	0.52	17.31	3.48	7.85	27.63	2.46	7.64	16.11	27.30	0.44	0.44	222
w113	BHOLE	0710806	8056043	842		3.01	1.30	34.54	0.11	145.77	101.84	5.42	23.45	37.15	27.70	6.40	0.66	333
w116	DWELL	0707199	8061517	827	7.5	1.19	1.10	13.51	48.80	15.58	19.59	1.57	20.92	13.50	25.80	6.80	0.52	260
w117	DWELL	0707165	8061820	826	11	2.40	5.86	167.10	0.00	147.64	276.05	2.68	27.12	3.62	26.40	6.90	1.79	896
w120	BHOLE	0704376	8062456	812		2.94	3.01	81.59	1.07	275.52					26.70		2.70	1344
w121	RBSED	0705355	8064078	812		0.34									18.90	6.90	0.25	124
w122 (2)	BHOLE	0710711	8056223	842		1.33	0.81	18.43	17.10	77.11	47.55	2.55	13.29	22.87	25.50	6.50	0.72	358
w123	BHOLE	0702518	8065761	800	56	1.86	1.71	38.97	0.00	345.58	241.61	6.92	14.24	15.63	27.00	7.10	1.94	968
w124	BHOLE	0699806	8063447	799		2.53	1.15	56.48	0.00	272.21	425.03	7.42	4.41	10.44	28.10	7.70	2.41	1200
w125	BHOLE	0698305	8062440	800		6.09					426.99	7.35	3.88	8.12	29.90	7.80	2.78	1387
w126 (2)	BHOLE	0714844	8049637	840		9.65	9.82	118.91	4.92	236.22	520.49	7.35	11.38	7.07	26.70	7.40	2.32	1155
w127	DWELL	0703500	8053138	847	48	1.25					186.45	3.35	8.29	16.65	27.70	7.40	1.50	752
w128	DWELL	0703777	8052251	850	10	0.82	0.58	119.19	77.78	11.17	188.99	1.37	6.33	3.90	27.20	7.50	1.31	655
w129	DWELL	0703758	8051885	852	10.5	0.60					227.80	32.55	30.33	30.75	27.80	7.40	1.62	807
w130	DWELL	0703868	8051735	852	15.5	0.22	0.00	169.88	1542.29	24.35	157.16	9.18	18.15	19.08	26.80	7.20	2.36	1173
w131	DAMWA	0699664	8051705	850		0.24	0.34	11.00	0.00	1.44	12.12	31.29	10.30	10.92	21.60	7.50	0.24	122
w132	DWELL	0698206	8052805	847	10.5	0.12					45.00	44.51	1.65	8.09	25.30	7.90	0.22	110.7
w133	DWELL	0698189	8052856	847	6.5	0.11	0.17	7.51	16.29	17.10	24.50	13.45	0.41	12.12	24.60	9.90	0.28	142
w134	SWELL	0711016	8051699	850	2.5	0.07	0.16	3.32	0.79	1.30	4.50	0.89	0.53	0.92	17.90	7.00	0.06	31
w136	SWELL	0711123	8051665	850	2.5	0.10					14.17	3.79	0.25	1.34	24.80	6.80	0.11	56.5

Water Sample ID	Water Source	Easting (UTM)	Northing (UTM)	Altitude (m)	SWL (m)	Ionic concentrations in mg/L									Temp (°C)	pH	E/C mS/cm	TDS (ppm)
						F^-(E)	F^-(C)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}				
w138	BHOLE	0696922	8053653	846		0.26	0.56	24.71	20.31	124.71	73.86	4.25	1.29	3.31	26.60	6.70	0.43	214
w139	DAMWA	0696673	8053831	846		0.29	0.37	20.18	36.12	2.39	3.28	82.30	7.70	29.63	23.50	7.80	0.54	269
w140	DWELL	0694891	8054999	845	7.5	0.42					290.71	1.02	5.19	8.39	26.10	7.40	1.78	891
w141	DWELL	0694563	8054731	848	10.5	0.26					130.41	5.23	3.05	14.72	27.60	7.90	0.81	401
w142	RBSED	0695985	8063570	792	0.3	0.32					4.84	141.42	54.13	34.78	22.20	6.70	0.81	[illegible]
w143	BHOLE	0690672	8070334	742		1.87	1.43	252.67	0.00	0.36	360.53	5.60	6.46	4.65	28.60	7.20	5.84	[illegible]
w144	BHOLE	0690792	8060935	778		0.50	1.32	100.33	0.00	283.27	78.79	4.48	17.15	9.83	27.20	7.00	1.85	921
w145	BHOLE	0688173	8055782	768	7	7.12	7.55	39.62	0.00	244.17	168.44	4.90	1.07	2.47	29.70	8.40	1.77	884
w146	DWELL	0688310	8055659	770	3	0.62	0.00	13.76	6.19	16.77	36.55	1.95	20.07	30.05	22.10	7.40	0.84	418
w147	DWELL	0688708	8055706	770	3	0.66					37.34	4.56	20.20	22.67	24.10	7.50	0.91	456
w148	DWELL	0688392	8055666	772	3	0.55	0.33	2.10	4.93	9.72	0.26	11.10	0.47	0.37	22.80	7.50	0.83	418
w149	DWELL	0688972	805551	782	7	1.94	1.40	12.07	1.49	1000.98	319.83	1.17	122.05	71.35	20.60	6.90	2.63	1319
w150 (2)	BHOLE	0709592	8031139	941		0.10	0.09	51.30	0.53	6.28	3.81	0.55	3.35	1.56	27.30	6.80	0.82	412
w151	BHOLE	0709087	80[illegible]4989	930		0.19	0.68	96.44	1.35	1199.60	40.59	2.17	29.15	38.24	27.30	6.60	0.89	447
w152	BHOLE	0712135	8037608	894	18.5	0.34					33.20	2.56	29.10	24.80	27.00	7.20	0.63	318
w153	DWELL	0711993	80[illegible]521	896	22.5	0.34	0.09	5.49	0.11	0.16	27.13	1.95	21.82	25.44	25.80	7.20	0.73	364
w154	BHOLE	0713568	80[illegible]729	894		0.21	0.24	44.73	1.53	1.66	79.77	4.39	[illegible]	9.97	25.50	7.00	0.96	480
w155	SWELL	0705465	8047842	864	2.5	0.19	0.23	3.73	14.61	7.90	9.20	4.78	0.70	5.38	22.50	6.80	0.11	557
w156	RBSED	0703466	8047730	857	2.5	0.35					4.71	5.37	1.88	10.15	21.80	7.20	0.86	346
w157	DWELL	0700486	8045898	836	12	1.15					260.14	99.48	18.93	17.52	25.60	7.50	1.93	962
w159	DWELL	0701970	8042143	899	34.5	0.23	0.22	3.70	0.99	3.61	15.59	1.04	7.18	10.95	27.80	7.00	0.88	439
w161	BHOLE	0704301	8038869	920		0.25	0.04	3.71	0.17	0.22					29.00	6.90	0.88	440
w162	DWELL	0704487	8037837	928	36	0.21	0.13	2.99	0.42	0.61	36.65	3.51	22.32	11.34	[illegible]	7.10	0.89	445
w163	DWELL	0704269	80[illegible]700	932	38	0.27					26.68	1.78	33.77	29.36	[illegible]	7.40	0.86	429
w164	DWELL	0705915	80[illegible]9407	915	26	0.27	0.19	146.96	795.87	10.12	99.68	2.42	19.20	7.86	29.00	7.40	1.45	726
w166	DWELL	0702115	8052549	860	15	0.20									25.10	6.50	0.84	420
w167	DWELL	0701976	80[illegible]2194	858	14.5	0.10									25.60	6.20	0.54	269
w168	DWELL	0699733	80[illegible]402	848	15.5	0.21									26.50	6.30	0.33	166
w174	BHOLE	0661387	8063514	650		0.68									29.00	6.80	0.99	496
w175	RBSED	0661921	80[illegible]002	650	0.5	0.33									26.60	6.70	1.05	530
w176	DWELL	0662021	8061563	650	11	7.44									27.80	7.80	8.56	4400
w177	DWELL	0661804	8057528	668	4.5	1.01									25.00	6.80	1.69	845
w178	DWELL	0661641	8056875	671	4	0.29									36.10	7.00	0.30	149

Water Sample ID	Water Source	Easting (UTM)	Northing (UTM)	Altitude (m)	SWL	Ionic concentrations in mg/L									Temp (°C)	pH	E/C mS/cm	TDS (ppm)
						F^- (E)	F^- (C)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}				
w179	DWELL	0661622	8056537	672	4	0.32									27.80	6.80	0.41	204
w191	DWELL	0661591	8048823	732		0.71									22.60	7.20	0.78	391
w192	SPRNG	0663274	8048322	733	1	0.65									24.10	6.50	0.56	[illegible]
w193	SPRNG	0663997	8049070	692	1	1.80									24.80	7.60	1.23	[illegible]
w194	DAMWA	0664742	8049080	702		0.52									25.70	8.80	0.38	[illegible]
w196	SWELL	0662765	8060904	654	1.5	0.16									26.20	5.20	0.12	61.7
w198	DWELL	0665004	8060167	656	10.5	0.27	0.00	8748.26	0.00	905.78	3468.15	17.78	319.92	17767.59	31.30	6.00	29.50	14750
w201	DWELL	0664446	8059965	657	4	0.75									27.30		1.03	468
w202	DWELL	0711146	8030494	930	21	0.38									27.80	7.10	1.10	547
w205	BHOLE	0702157	8074685	787	18	0.73	0.28	233.93	0.00	16.23	127.16	2.77	19.25	33.54	24.80	6.80	1.69	843
w206	BHOLE	0702303	8074439	787	18	0.69	0.12	20.96	3.61	38.28					29.40	6.50	1.15	573
w207	BHOLE	0702144	8074620	787	18	0.73	0.26	0.24	0.00	26.87	85.60	2.56	19.97	42.19	25.10	6.90	1.19	596
w208	SWELL	0702183	8072106	790	2.5	0.29	0.21	6.07	5.93	5.88	8.78	1.65	1.72	3.24	24.20	6.80	0.08	41.1
w209	BHOLE	0700244	8067928	793		0.77	0.31	59.55	0.00	3.94	74.05	3.12	41.15	36.29	30.30	6.70	1.03	514
w210	BHOLE	0708041	8064737	818	14	0.59	0.29	22.57	0.25	11.77	61.98	3.70	15.90	15.91	30.30	6.70	0.79	397
w211	BHOLE	0710178	8065835	818	27	0.63	0.31	323.49	7.75	78.62	0.00	0.00	0.00	0.00	30.40		1.94	969
w212	DWELL	0710401	8065870	818	6.5	1.13	0.23	38.30	1.53	1.66	93.94	14.29	30.31	19.26	29.60	7.00	0.91	454
w213	BHOLE	0715254	8065642	814		0.49	0.11	118.50	1.63	5.12	36.94	1.59	22.46	51.94	[illegible]	[illegible]	1.22	607
w214	BHOLE	0717053	8065143	814	5.2	0.38									[illegible]	[illegible]	0.56	279
w215	BHOLE	0717377	8065486	817		0.36									27.70	7.70	0.57	288
w216	BHOLE	0717539	8067645	828		0.42	0.87	1016.17	0.00	7.55	73.54	2.58	82.32	454.33	28.70	6.30	4.73	2370
w217	BHOLE	0715876	[illegible]	226		1.00	0.81	632.36	0.00	2.52	64.51	1.45	76.27	87.79	28.10	6.90	2.56	1277
w218	BHOLE	0713429	8064529	819		1.34	0.47	26.16	7.50	1.88	3.26	0.11	49.92	4.11	28.70	6.90	1.05	[illegible]
w220	DWELL	0716037	8044514	868	21.5	0.28									27.10	6.90	1.24	620
w221	SWELL	0716055	8044502	865	4	0.49	0.67	9.23	6.01	2.16	12.01	5.27	1.86	12.06	21.40	7.40	0.17	82
w222	BHOLE	0716461	8044417	869		0.43	0.00	41.47	4.46	54.27	67.81	8.42	17.29	59.05	28.10	6.20	0.74	371
w223	BHOLE	[illegible]	8047131	864	30	1.80									27.80	7.00	0.96	481
w224	BHOLE	0718553	8047784	858		2.52	0.64	7.74	0.00	30.33	[illegible]	0.08	1.60	1.40	29.70	6.90	1.11	553
w225	BHOLE	0717641	8050201	846		4.40	2.40	56.84	0.04	76.04	[illegible]	1.99	4.10	14.73	28.00	7.10	1.84	919
w226	DAMWA	0721591	8050295	855		0.22									30.30	8.20	0.21	103.2
w227	DAMWA	0721639	8050541	855		0.27					3.08	5.27	1.86	12.06	21.90	7.60	0.20	100
w229	BHOLE	0726810	8053885	872		0.99	0.04	90.26	5.98	0.20	60.84	1.50	19.99	16.93	24.30	7.50	0.91	460
w230	BHOLE	0726907	8057678	852	9.2	0.98	0.38	122.19	9.09	3.68	110.65	1.80	49.07	30.63	30.30	6.70	1.46	736

Water Sample ID	Water Source	Fasting (UTM)	Northing (UTM)	Altitude (m)	SWL (m)	Ionic concentrations in mg/L									Temp (°C)	pH	E/C mS/cm	TDS (ppm)
						F⁻(E)	F⁻(C)	Cl⁻	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}				
w231	BHOLE	0729971	8061839	864		0.83	0.00	251.45	0.00	1.95	81.75	2.07	27.63	27.54	24.50	6.80	1.60	801
w232	BHOLE	0729590	8061539	870	34.1	1.35	0.05	6.07	0.11	1.25	121.98	2.63	17.15	10.45	[illegible]	7.00	1.09	541
w235	BHOLE	0734004	8065019	824		0.24	0.18	1.03	0.13	0.59	12.19	1.02	10.29	14.61	23.80	7.00	0.44	222
w237	BHOLE	[illegible]	8067311	812		0.24	0.24	0.06	2.59	0.81	12.76	0.57	5.44	6.18	26.70	6.80	0.20	100
w238	BHOLE	0732434	8065732	810		2.71	2.44	27.44	0.00	10.99	129.27	54.10	27.86	30.08	[illegible]	7.00	1.10	554
w239	BHOLE	0726883	8068282	826		0.55	2.41	20.39	0.00	1.76	141.13	3.18	1.53	6.56	25.60	6.90	0.98	491
w240	BHOLE	0725690	8067679	833		0.55	0.20	6.48	8.80	3.44	84.50	2.65	18.42	2.72	25.60	6.90	0.98	491
w241	BHOLE	0722371	8066868	842	12.9	0.58	0.14	51.67	4.15	5.09	133.99	1.58	32.37	36.02	25.40	6.80	1.20	601
w245	BHOLE	0720239	8066052	836		0.47	0.19	2.42	0.97	3.87	56.87	2.08	21.43	4.74	24.10	7.30	0.64	321
w246	DWELL	0720783	8066133	839	16	0.59	0.14	6.48	0.07	3.38					26.20	7.10	0.91	454
w247	DWELL	0720582	8066770	841	13	0.58	0.00	31.40	0.00	4.53					27.00	[illegible]	1.33	665
w248	SWELL	0720248	8067495	843	1	0.11									21.30	7.30	0.06	[illegible]
w249	BHOLE	0720727	8068325	848		0.50									27.50	6.50	3.61	[illegible]
w250	BHOLE	0721281	[illegible]	251		0.53	0.22	143.72	0.00	0.90					27.80	6.60	1.62	[illegible]
w252	BHOLE	0719704	[illegible]	978		0.20	0.59	0.00	0.00	22.26					30.20	6.80	0.93	467
w253	BHOLE	0722080	[illegible]	967		0.23	0.91	51.39	0.53	6.28	64.14	4.38	29.72	11.58	29.70	6.70	1.10	551
w254	SWELL	0711583	8017864	1035	1.5	0.17	0.06	3.18	0.08	0.25					26.50	6.80	0.65	327
w255	FSTRM	0711594	8017829	1035		0.23	2.59	2.84	0.44	69.71	11.78	2.80	24.08	48.39	[illegible]	7.30	0.56	284
w256	SWELL	0711598	8017853	1036	2.5	0.16									[illegible]	7.20	0.63	321
w257	SWELL	0710087	8016285	1058	1.5	0.49									24.30	7.30	0.86	431
w258	SWELL	0710043	8014518	1092	1	0.27	0.09	0.34	9.99	3.46	10.97	0.14	18.85	15.46	20.00	6.90	0.42	210

Appendix 2: ZINWA Water Analysis Results

This Appendix gives routine water analysis results obtained from ZINWA. The analyses were conducted in the 1980s and 1990s and the corresponding sample number used in this thesis is given for reference. 'None' under 'This Thesis' indicates boreholes which were in disrepair at the time of this Survey.

Sample ID		Ionic concentrations in mg/L									Alkalinity (to methyl orange as $CaCO_3$mg/L)	Total Hardness (as $CaCO_3$ mg/L)	Ec (mS cm^{-1})	TDS (mg/L)
ZINWA	This Thesis	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-				
zs01	w224		25.86	0.89	291.40	156.50	7.60	6.00	38.70	507.90	416.33	153,53	0.89	521.8
zs02	w004		36.30	1.40	0.00	272.00	3.90	2.00	5.60	725.40	594.6	18.10	1.27	744.1
zs03	w232		3.99	0.73	3.70	76.00	2.44	14.00	36.65	656.80	538.38	158.81	0.96	564.5
zs05	w230	0.90	7.73	0.40	2.49	78.00	0.89	26.00	95.79	613.60	502.96	329.12	0.89	520.6
zs06	w214		2.11	6.70	1.88	24.00	2.11	15.00	45.40	5.41	270.71	[illegible]	0.49	[illegible]
zs07	w096		1.00	0.29	9.00			37.00	112.00		379.00	[illegible]		[illegible]
zs08	w040	0.16	9.00	115.00	115.00			76.06	0.00		443.00	550.00		632.6
zs10	none	2.80	43.00	14.00	21.00			28.00	113.40		457.00	258.00		925
zs11	nonc	2.80	87.30	8.40	56.50	618.90	14.80	7.50	17.10	1610.00	1320.00	75.40	0.12	68.4
zs16	w061	4.00	42.20	0.10	3.30	290.00	7.10	0.50	8.10	775.40	635.60	27.20	0.11	625.4
zs17	w217		25.70	0.70	7.50	72.00	1.40	26.00	66.40	477.90	391.70	272.20	0.93	544.2
zs18	w249		22.80	0.50	1.30	90.00	0.70	15.00	124.10	692.10	567.30	388.90	0.86	502.5

Appendix 3: Boreholes Not Sampled

Although in this study it was intended to sample all water supply boreholes, some were not sampled because the water pumps were derelict. Two of the boreholes had, however, been previously sampled by ZINWA (refer to Appendix 2). The locations of these boreholes as determined with a GARMIN 12 GPS are given below:

Borehole Count	Easting	Northing	ZINWA Sample ID
1	0703930	8040142	
2	0698989	8032963	
3	0705592	8064734	
4	0699433	8047139	
5	0714365	8053061	
6	0712083	8051579	
7	0712100	8040332	
8	0725340	8050407	
9	0732444	8061201	
10	0731809	8060987	
11	0727293	8066317	
12	0735731	8066281	
13	0707770	8060271	
14	0686800	8014900	zs10
15	0705355	8064078	zs11

Appendix 4: Raw Stratigraphic Log Data

Log Data from ZINWA

Raw log data obtained from the Zimbabwe National Water Authority (ZINWA) and used in this thesis are shown 'as is' (from disk) in this appendix. It must be noted that the data are lithology data only. The stratigraphic interpretations discussed in the thesis were performed by Mamuse (this thesis) with contributions of Ait-Kaci Ahmed (*in prep.*; pers. comm.).

A hydrogeologist at ZINWA pointed out that the coordinates used in the location of boreholes were only approximate. Therefore, while these approximate coordinates are shown in this appendix, the correct coordinates as determined with the aid of a GARMIN 12 GPS are quoted in the text of this thesis and can also be read off Appendix 1. In the data below, the collar elevations of the boreholes read '0.00' because they were not determined by ZINWA. However, in the current project, the elevations were determined from the topographic map datum by Spline interpolation in ArcView® GIS and are shown in Appendix 1. Under 'hole' in the data below, the figures to the left represent depths from the ground level, and numbers to the right, represent bore width, according to the ZINWA hydrogeologist.

In this thesis, the ZINWA names for boreholes have been dropped in favour of shorter ones. The table below matches the ZINWA names to those used in this thesis, and gives the Sample ID for easy reference to Appendix 1.

Borehole Name		**Sample ID**	**Easting**	**Northing**
This thesis	*ZINWA*			
B3	6-GO-N-091	w017	702407	8025[illegible]
B5	6-GO-S-174	w050	669080	8032829
B6	6-GO-N-090	w093	693034	8032111
B7	6-GO-S-095	w107	685520	8014309
B9	6-GO-S-184	w103	6[illegible]	8050575

```
WELL: 6-GO-N-091
LOC: Gurawakanya Sec School
X: 703000
Y: 8025400
ELEV:    0.00
LITH:
      6.000 MUDSTONE Mudstone, brownish
     97.000 SHALE Shale, greyish
    120.000 SAND Course sand
    121.000 SHALE Shale
HOLE:
     12.480      203.000
    121.000      150.000
CASING:
     12.480      150.000
ANNULUS:
     12.480 UNSPEC
WELL: 6-GO-S-174
LOC: Siayaurembo
X:   6691
Y:   80332
```

```
ELEV:    0.00
LITH:
       2.000 TOPSOIL Topsoil, brownish
      20.000 CLAY Silty clay, brownish
      25.000 MUDSTONE Mudstone, greyish
      30.000 SAND Course sand with mudstone
     154.000 MUDSTONE Mudstone with touches of shale
     225.000 SHALE Shale with mudstone
     299.000 MUDSTONE Mudstone with touches of shale
     306.000 SAND Medium coarse sand
     311.000 SANDCLAYEY Sand clayey, greyish
HOLE:
      90.000      306.250
     311.000      150.000
CASING:
      90.000      150.000
SCREEN:
      24.000       30.000
      36.000       42.000
ANNULUS:
      90.000 QUARRY



WELL: 6-GO-N-090
LOC: DENDA CLINIC
X: 693200
Y: 8031900
ELEV:    0.00
SWL:  55.00
LITH:
       3.000 SAND Sand, reddish (Escarpment grit)
      73.200 MUDSTONE Mudstone,greyish (Madumabisa)
     235.600 SHALE Shale, blackish with\coal (Madumabisa)
     260.300 SANDSTONE Sandstone, whitish\(Upper Wankie)
HOLE:
      25.100      213.000
     260.300      156.250
CASING:
      25.100      175.000
     260.300      113.000
SCREEN:
     236.300      260.300
ANNULUS:
     236.300 UNSPEC


WELL: 6-GO-S-095
LOC: SESAMI BAPTIST MISSION
X: 683400
Y: 8015200
ELEV:    0.00
LITH:
      21.300 ALLUVIUM Sandy alluvium
     190.800 MUDSTONE Madumabisa mudstone, greyish
```

```
     201.500 SANDSTONE Upper Wankie sandstone,\whitish, medium
grained
     210.600 MUDSTONE Mudstone
     228.900 SAND Medium grained sand, whitish
HOLE:
      18.300      203.000
     228.900      156.500
CASING:
      18.300      175.000
     228.900      100.000
SCREEN:
     210.000      228.000
ANNULUS:
     228.900 UNSPEC
```

```
WELL: 6-GO-S-184
LOC: Madzivazvido Clinic
X: 660300
Y: 8031300
ELEV:    0.00
LITH:
      70.000 SAND Sand
      90.000 SANDSTONE Sandstone
HOLE:
      39.000      152.000
      90.000      125.000
CASING:
      39.000      125.000
SCREEN:
      24.000       36.000
ANNULUS:
       2.000 SANSEAL
      39.000 UNSPEC
```

Other sources of log data

The log data obtained from Lepper (1992) and Garande (1990) were read off constructed hard-copy lithostratigraphic logs. New logs were then re-constructed using ROCKWORKS software.

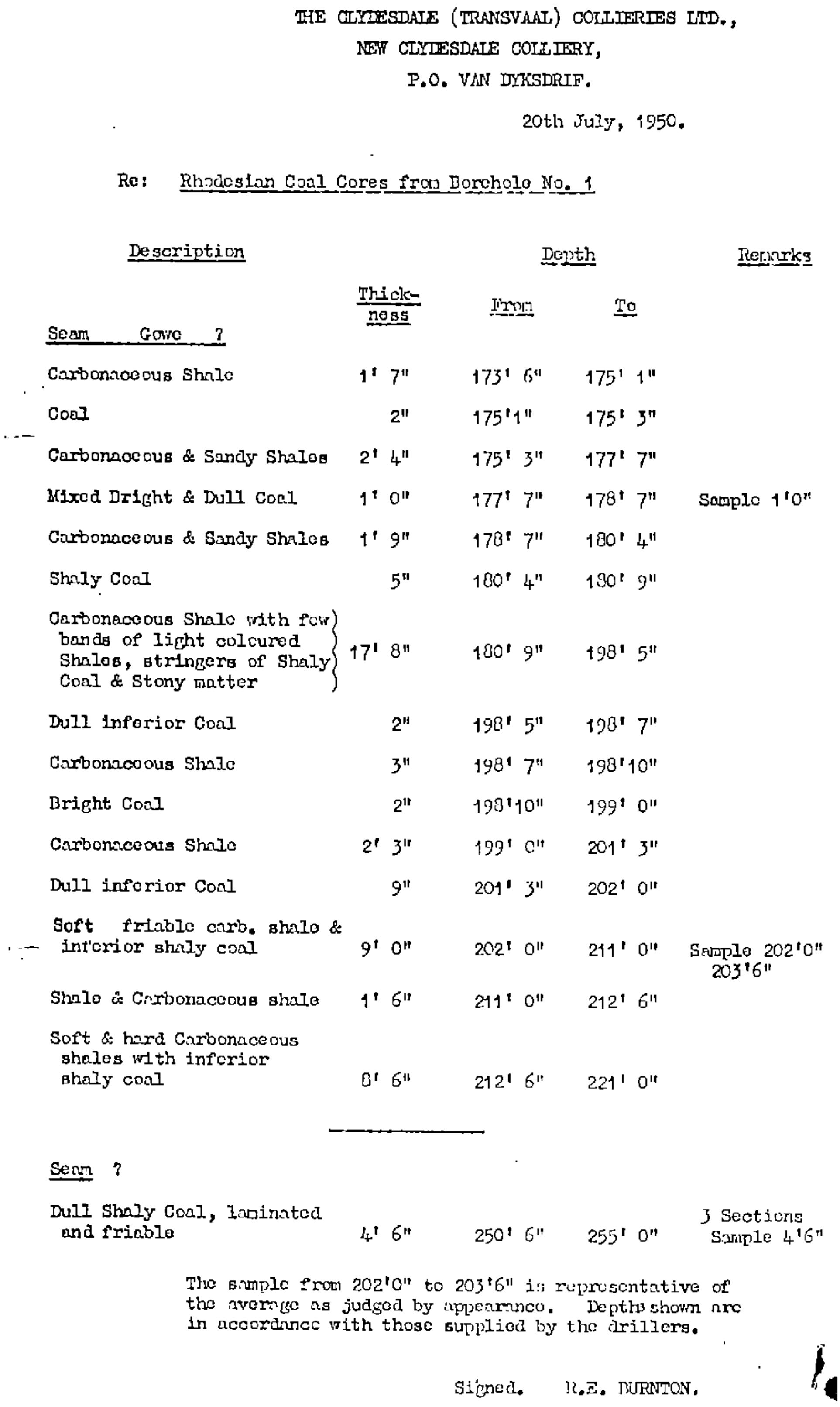
The log data pertaining to a borehole of Global Literature Life Boreholes (1990) were obtained from a file of raw lithologic data.

Appendix 5: Coal Stratigraphic and Analysis Data

This Appendix is concerned with the original stratigraphic sampling records of Middle Wankie coal seams as determined during coal exploration, and the accompanying results of coal proximate analysis. The samples were collected from the following boreholes (with names used in this thesis given in brackets): WB1 (B12), WB2 (B16), WB8 (B14), WB9 (B15). The information was obtained from *Report on prospecting in eastern Sebungwe* (1951).

The results of proximate analysis of a Lower Madumabisa coal sample (*Report on prospecting in eastern Sebungwe* 1951) and those of ultimate analysis of a coal sample from the study area of unspecified seam and location (Bohmke & Duncan 1974) are also included.

Borehole WB1 (B12): Coal Seam Log



THE CLYDESDALE (TRANSVAAL) COLLIERIES LTD.,
NEW CLYDESDALE COLLIERY,
P.O. VAN DYKSDRIF.

20th July, 1950.

Re: Rhodesian Coal Cores from Borehole No. 1

Description	Thickness	Depth From	Depth To	Remarks
Seam Gowe ?				
Carbonaceous Shale	1' 7"	173' 6"	175' 1"	
Coal	2"	175'1"	175' 3"	
Carbonaceous & Sandy Shales	2' 4"	175' 3"	177' 7"	
Mixed Bright & Dull Coal	1' 0"	177' 7"	178' 7"	Sample 1'0"
Carbonaceous & Sandy Shales	1' 9"	178' 7"	180' 4"	
Shaly Coal	5"	180' 4"	180' 9"	
Carbonaceous Shale with few bands of light coloured Shales, stringers of Shaly Coal & Stony matter	17' 8"	180' 9"	198' 5"	
Dull inferior Coal	2"	198' 5"	198' 7"	
Carbonaceous Shale	3"	198' 7"	198'10"	
Bright Coal	2"	198'10"	199' 0"	
Carbonaceous Shale	2' 3"	199' 0"	201' 3"	
Dull inferior Coal	9"	201' 3"	202' 0"	
Soft friable carb. shale & inferior shaly coal	9' 0"	202' 0"	211' 0"	Sample 202'0" 203'6"
Shale & Carbonaceous shale	1' 6"	211' 0"	212' 6"	
Soft & hard Carbonaceous shales with inferior shaly coal	8' 6"	212' 6"	221' 0"	
Seam ?				
Dull Shaly Coal, laminated and friable	4' 6"	250' 6"	255' 0"	3 Sections Sample 4'6"

The sample from 202'0" to 203'6" is representative of the average as judged by appearance. Depths shown are in accordance with those supplied by the drillers.

Signed. R.E. BURNTON.

ANNEXURE "B"

ANALYSIS OF SAMPLES FROM RHODESIA BORE

	177'/178'	202'/203'6"	250'6"/252'	252'/253'6"			253'6"/255'
				1.	2.	3.	
Volatile Matter	35.4%	16.30%	25.40%	27.50%	42.80%	24.40%	30.30%
Fixed Carbon	35.5	31.60	50.20	40.40	35.70	39.90	39.10
Ash	12.9	42.40	9.50	18.50	5.40	23.40	18.90
Water	16.2	9.70	14.90	13.60	16.10	12.30	11.70
Sulphur	0.92	-	-	-	0.34	-	-

Note: All samples were non-coking with no evidence of coherence of particles.

When preparing samples 202'/203'6" it was observed that the sample contained pieces of pyrites indicating that the bore had passed through a rib of pyrites.

Sample at 252'/253'6" was divided into (1) average of good looking pieces, (2) selected good pieces and (3) average of poor looking pieces.

Borehole WB2 (B16): Coal Seam Log

SAMPLING RECORD

BOREHOLE NO. W.B.2.

Seam No. 2. ?

Diameter of Core: $1\frac{3}{8}$" Diameter.

Core received in Johannesburg on the 29th June, 1951.

Core split for sampling on the 2nd July, 1951.

The Core as received, had been divided into six sections and marked as follows:-

Top.	788' - 7"	to	792' - 1"	(24" missing)
	792' - 1"	to	793' - 7"	(1" missing)
	793' - 7"	to	795' - 1"	
	795' - 1"	to	796' - 7"	(1" missing)
	796' - 7"	to	798' - 0"	
	798' - 0"	to	799' - 2"	
Floor.				

SAMPLING:

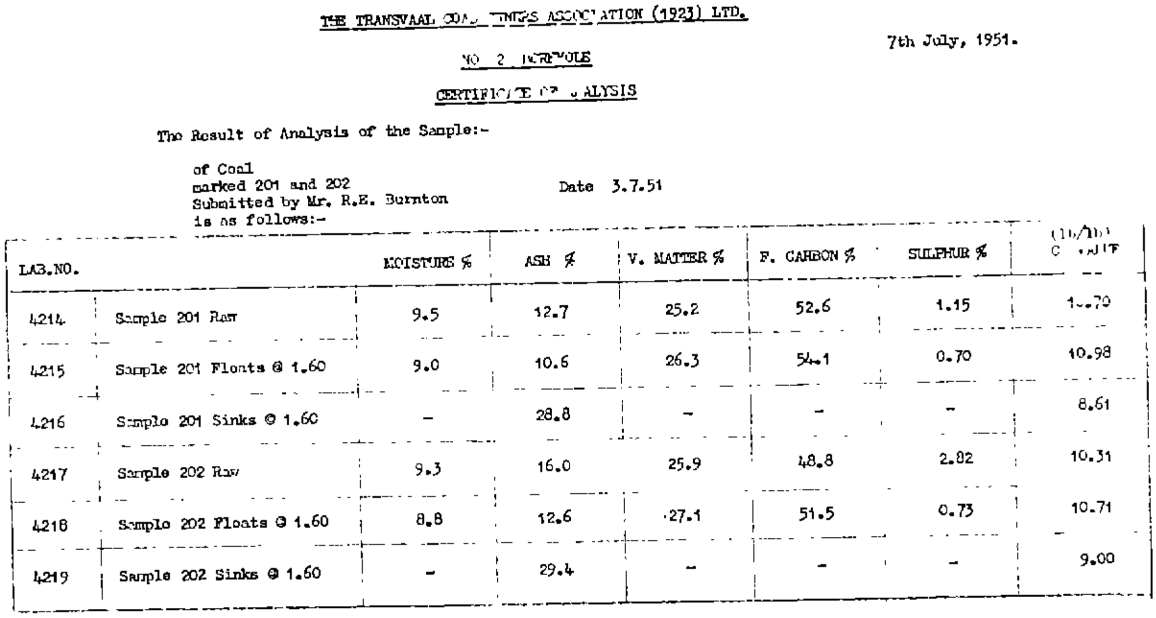
Sample No.	From	To	Sample Width	Description
201	788' - 7"	794' - 7"	6' - 0"	Dull, Laminated Coal with narrow pyritic band 1'3" from the top of sample. Weathered appearance and tends towards a carbonaceous shale. (25" of core missing).
202	794' - 7"	799' - 2"	4' - 7"	Dull, very friable coal, of slate-grey lustre. Three $\frac{1}{4}$" wide pyritic and shaly bands occur in the bottom 1'4". (1" of core missing).

Half the core has been prepared for samples 201 and 202, the remainder has been repacked in sequence.

Signed: R.E. BURNTON.

TECHNICAL ASSISTANT.

Borehole WB2 (B16): Coal Proximate Analysis



THE TRANSVAAL COAL OWNERS ASSOCIATION (1923) LTD.

7th July, 1951.

NO. 2 BOREHOLE

CERTIFICATE OF ANALYSIS

The Result of Analysis of the Sample:-

of Coal
marked 201 and 202
Submitted by Mr. R.E. Burnton
is as follows:-

Date 3.7.51

LAB.NO.		MOISTURE %	ASH %	V. MATTER %	F. CARBON %	SULPHUR %	(lb/lb) C [illegible]
4214	Sample 201 Raw	9.5	12.7	25.2	52.6	1.15	10.70
4215	Sample 201 Floats @ 1.60	9.0	10.6	26.3	54.1	0.70	10.98
4216	Sample 201 Sinks @ 1.60	-	28.8	-	-	-	8.61
4217	Sample 202 Raw	9.3	16.0	25.9	48.8	2.82	10.31
4218	Sample 202 Floats @ 1.60	8.8	12.6	27.1	51.5	0.73	10.71
4219	Sample 202 Sinks @ 1.60	-	29.4	-	-	-	9.00

Borehole WB8 (B14): Coal Seam Log

SAMPLING RECORD

BOREHOLE NO. W.B.8

Diameter of core 1$\frac{3}{8}$"

Core received at New Clydesdale 26.9.51

The core, as received, had been divided into the following sections and packed in paper bags. The core was extensively ground and no identification according to strata in the seam was possible. Half of each bag was used for sampling purposes.

	From	To	Width	Remarks	Sample No.
Roof.	304'0"	305'0"	1'0"	Dull, Shaly coal	801
	305'0"	306'0"	1'0"	" " "	802
	306'0"	307'0"	1'0"	" " "	803
	307'0"	312'0"	5'0"	Missing	-
	312'0"	313'0"	1'0"	Dull, Shaly Coal	804
	313'0"	314'0"	1'0"	" " "	805
	314'0"	315'0"	1'0"	" " "	806
	315'0"	316'0"	1'0"	" " "	807
	316'0"	320'0"	4'0"	Missing	-
	320'0"	321'0"	1'0"	Dull, Shaly Coal	808
	321'0"	322'6"	1'6"	" " "	809

Total: 18'6" Seam Width

Total: 9'6" Recovered core length

Borehole WB8 (B14): Coal Proximate Analysis

THE TRANSVAAL COAL OWNERS ASSOCIATION (1923) LTD.

P.O. BOX 1197,
JOHANNESBURG.

BOREHOLE NO. W.B. 8 — 8th October, 1951.

CERTIFICATE OF ANALYSIS

The result of analysis of sample:

of COAL EX THE CLYDESDALE (TRANSVAAL) COLLIERIES, LIMITED.

Submitted by MR. R.E. BURNTON.

is as follows:-

LAB.NO.		MOISTURE %	ASH %	V.MATTER %	F.CARBON %	C.V.(LBS./LB)
6546	Sample No. 801	8.2	33.4	20.1	38.3	6.61
6547	" " 802	7.3	31.5	24.0	37.2	7.06
6548	" " 803	8.9	22.4	21.9	46.8	8.33
6549	" " 804	8.4	19.9	23.9	47.8	8.93
6550	" " 805	9.4	16.3	23.1	51.2	9.28
6551	" " 806	9.1	14.2	24.2	52.5	9.80
6552	" " 807	8.0	20.0	26.5	45.5	9.37
6553	" " 808	7.3	37.3	19.9	45.5 (35.5)?+	6.43
6554	" " 809	6.9	41.4	18.5	33.2	6.00

The Managing Director,
The Clydesdale (Transvaal) Collieries Ltd.,
P.O. Box 1948,
JOHANNESBURG.

+ This analysis addes up to 110. F. Carbon 45.5 should probably read 35.5.

Borehole WB9 (B15): Coal Seam Log

SAMPLING RECORD

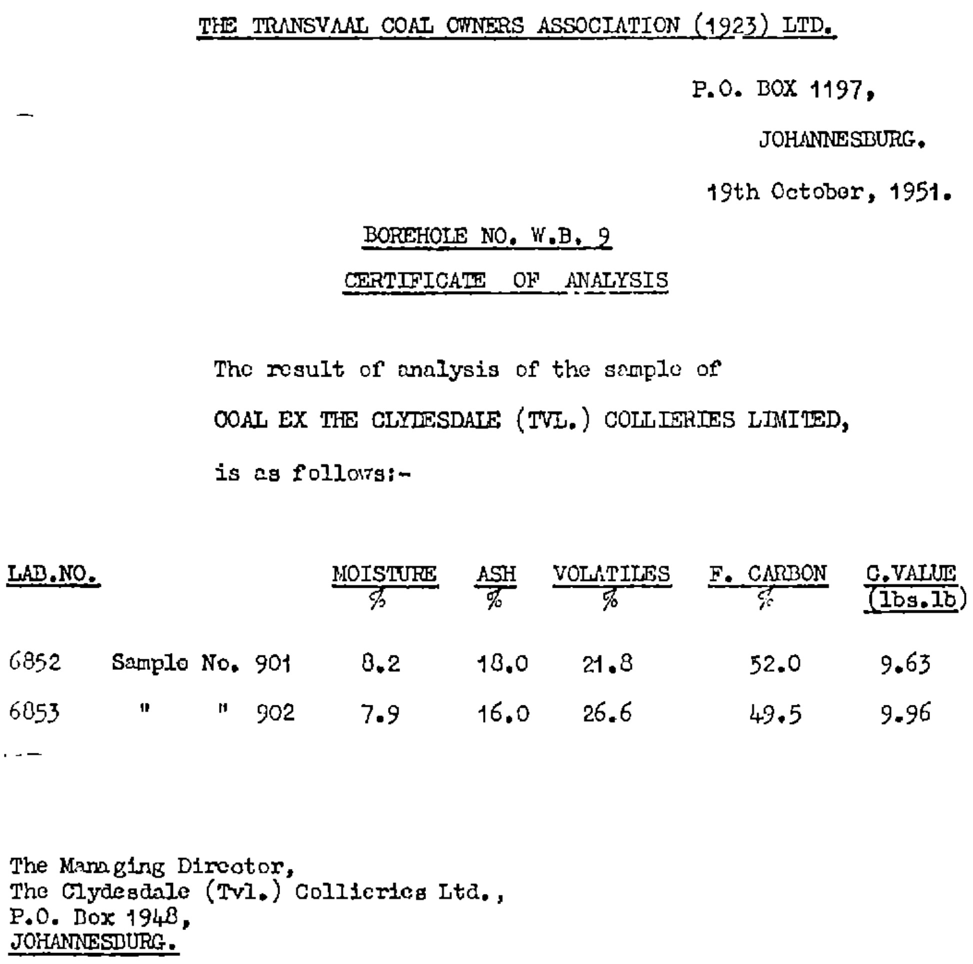
BOREHOLE NO. W.D. 9.

Diameter of Core: 1$\frac{3}{8}$"

Core received at New Clydesdale: 26.10.51

Sample No.	From	To	Width	Remarks
901	502' 9"	506' - 0"	3' - 3"	Soft, friable, dull coal. 1" Sandstone band from 504'6" to 504'7" (excluded from sample)
902	506' 0"	509' - 2"	3' - 2"	Soft, friable, dull coal. 3" of pyritic sandstone from 507'0" to 507'3" (excluded from sample) 2" pyritic band from 508'10" to 509'0" (excluded from sample)
		Total Width	6' - 5"	
		Recovery	100%	

Borehole WB9 (B15): Coal Proximate Analysis



THE TRANSVAAL COAL OWNERS ASSOCIATION (1923) LTD.

P.O. BOX 1197,
JOHANNESBURG.
19th October, 1951.

BOREHOLE NO. W.B. 9

CERTIFICATE OF ANALYSIS

The result of analysis of the sample of
COAL EX THE CLYDESDALE (TVL.) COLLIERIES LIMITED,
is as follows:-

LAB.NO.		MOISTURE %	ASH %	VOLATILES %	F. CARBON %	C.VALUE (lbs.lb)
6852	Sample No. 901	8.2	18.0	21.8	52.0	9.63
6853	" " 902	7.9	16.0	26.6	49.5	9.96

The Managing Director,
The Clydesdale (Tvl.) Collieries Ltd.,
P.O. Box 1948,
JOHANNESBURG.

Lower Madumabisa Coal Sample Analysis

The proximate analytical results of a sample (location unspecified) of a Lower Madumabisa coal sample (*The report on prospecting operation in eastern Sebungwe* 1950) are as follows:

Ash	36.36%
Moisture	8.2%
Volatile Matter	37.3%
Fixed Carbon	18.15%
Fuel Factor	0.5 (lb.lbs)
Calorific Value	-

'Gokwe Coal' Sample Analysis

A sample from an unspecified location and seam, just named 'Gokwe Coal' gave the following ultimate analysis results (Bohmke & Duncan 1974):

Carbon	60.50%
Hydrogen	2.88%
Nitrogen	1.46%
Total Sulphur	0.51%
Oxygen	-

[The percentage of hydrogen was not given, but historically it is determined by subtracting the sum of the other components of ultimate analysis from 100 (Speight 1994)]

The mineral matter content of the sample (determined from the mineral ash after combustion) was as follows:

Constituent	w/w %
SiO_2	34.55
Al_2O_3	26.66
Fe_2O_3	13.47
CaO	10.49
MgO	1.52
Na_2O	1.43
K_2O	0.07
SO_3	5.61
P_2O_5	2.24
TiO_2	1.30
Cl	0.28

(The constituents add to 97.62%, suggesting that the results may not be complete).