

**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. Wilmore 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

<b>ACKNOWLEDGEMENTS</b>	<b>i</b>	
<b>LIST OF ILLUSTRATIONS</b>	<b>v</b>	
<b>ABBREVIATIONS USED IN THIS THESIS</b>	<b>vii</b>	
<b>ABSTRACT</b>	<b>viii</b>	
<b>CHAPTER 1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Background To Study	1
	1.2 Fluorine and Health: Selected Case Histories	2
	1.3 Fluorosis in Zimbabwe: Previous Work	6
	1.4 Purpose and Significance of This Study	7
<b>CHAPTER 2</b>	<b>THE STUDY AREA</b>	<b>9</b>
	2.1 Location of the Study Area	9
	2.2 Relief	11
	2.3 Climate	13
	2.4 Geology	13
	2.4.1 Geology of the Central Part of the Study Area	13
	2.4.2 Geology of the Eastern Part of the Study Area	20
	2.5 Hydrogeology	21
	2.5.1 Drainage	21
	2.5.2 Groundwater	21
<b>CHAPTER 3</b>	<b>FLUORINE IN THE ENVIRONMENT</b>	<b>28</b>
	3.1 THE GEOCHEMISTRY OF FLUORINE	28
	3.1.1 Fluorine Abundance in Rock-forming Minerals	28
	3.1.2 Fluorine Abundance in Igneous Rocks	29
	3.1.3 Behaviour of Fluorine in Magmatic Processes	30
	3.1.4 Fluorine Abundance in Metamorphic Rocks	32
	3.1.5 Fluorine in Weathering Processes	33
	3.1.6 Fluorine Abundance in Natural Waters	34
	3.1.7 Fluorine in the Atmosphere	36
	3.1.8 Fluorine Abundance in Sedimentary Rocks	36

	3.2 FLUORINE AND HUMAN HEALTH	38
	3.2.1 The Bioavailability of Fluoride	38
	3.2.2 The Biochemical Function of Fluoride	40
	3.2.4 Manifestations of Endemic Fluorosis	42
	3.2.4 Fluoride Exposure	47
<b>CHAPTER 4</b>	<b>METHODS OF STUDY</b>	<b>52</b>
	4.1 SAMPLING PROCEDURES	52
	4.1.1 Sample Preparation	52
	4.1.2 Sample Holding Times and Preservation	53
	4.1.3 Sample Containers	54
	4.2 ANALYTICAL METHODS	56
	4.2.1 Ion Selective Methods-Overview	56
	4.2.2 The Fluoride (and other) ISE	57
	4.2.3 The FISE Protocol Used in This Study	68
	4.2.4 High Performance Ion Chromatography (HPIC)	71
	4.3 COMPUTER- BASED METHODS	72
	4.3.1 Initial Data Capture	72
	4.3.2 GIS Manipulation	72
	4.3.3 Other Computer Programs	73
<b>CHAPTER 5</b>	<b>RESULTS OF THE STUDY</b>	<b>74</b>
	5.1 Overview of Results	74
	5.2 Fluoride Concentrations	75
	5.3 Major Ion Concentrations and TDS	79
	5.4 Bari Salt Pan Samples	82
<b>CHAPTER 6</b>	<b>DISCUSSION</b>	<b>83</b>
	6.1 GEOLOGY AND FLUORIDE DISTRIBUTION	83
	6.1.1 Fluoride Distribution in the Central Part of The Study Area	85
	6.1.1.1 Superficial Deposits and Fluoride Distribution	86
	6.1.1.2 The Upper Karoo and Fluoride Distribution	87
	6.1.1.3 The Lower Karoo and Fluoride Levels	89
	6.1.1.4 Geology and Fluoride Distribution in the Central Part of the Study Area: A Synopsis	102
	6.1.2 Fluoride Distribution in the Eastern Part of the Study Area	110

6.2 FLUOROSIS RISK MAP	113
6.2.1 Rationale, Assumptions and Limitations of Interpolation	114
6.2.2 Fluorosis-Risk Map Based on Data From all Water Sources	115
6.2.3 Fluorosis-Risk Map Based on Borehole Data Only	118
6.2.4 Differences Between The Two Maps	119
6.2.4.1 Visual Appearance	119
6.2.4.2 Interpretation, Limitations and Applications	120
6.2.5 The fluorosis Risk Map: Implications for Health	121
6.3 MAJOR IONS AND TDS	125
6.4 FLUORIDE AND PH	135
6.5 MAJOR IONS, TDS, PH AND F CONTAMINATION: A SYNOPSIS	136
<b>CHAPTER 7</b>	<b>RECOMMENDATIONS AND CONCLUSIONS 140</b>
7.1 REMEDIAL MEASURES	140
7.1.1 Avoiding Fluoride-rich Water	140
7.1.2 Treating Fluoride-rich Water	144
7.1.2.1 Sorption methods	144
7.1.2.2 Contact Precipitation Methods	145
7.1.2.3 Flocculation Methods: The Nalgonda Technique	146
7.1.2.4 F <sup>-</sup> Removal Strategies: Applicability to Gokwe	146
7.1.3 Remedial Methods: Concluding Remarks	148
7.2 CONCLUSIONS	149
7.3 FURTHER RESEARCH	152
<b>REFERENCES</b>	<b>155</b>
<b>APPENDICES</b>	<b>164</b>
Appendix 1: Water Sample Attributes	164
Appendix 2: ZINWA Water Analysis Results	171
Appendix 3: Boreholes Not Sampled	172
Appendix 4: Raw Stratigraphic Log Data	173
Appendix 5: Coal Stratigraphic And Analysis Data	176

## LIST OF ILLUSTRATIONS

### FIGURES

2.1	Location of the Study Area	10
2.2	Topography of the Study Area	12
2.3	Geological Map of the Central Part of the Study Area	14
2.4	Diagrammatic Section of the Sengwa Sub-basin	15
2.5	Geological Map of the Eastern Part of the Study Area	22
2.6	Water Level Contour Map of the Study Area	23
5.1	Correlations Between HPIC and FISE Fluoride Determinations	75
5.2	Frequency Percent of Fluoride Concentration Ranges	77
5.3	Breakdown of Water Source Types by Fluoride Concentration	78
5.4	Breakdown of Fluoride Concentration Ranges by Water Source	79
5.5	Pie Chart of Water Quality with respect to WHO Guidelines	81
6.1	Geology and Fluoride Distribution in the Central Part	84
6.2	Lithostratigraphic Log of Borehole B6	88
6.3	Lithostratigraphic Log of Borehole B7	94
6.4	Lithostratigraphic Log of Borehole B8	95
6.5	Lithostratigraphic Correlation of Boreholes B7 and B8	96
6.6	Lithostratigraphic Log of Borehole B11	98
6.7	Lithostratigraphic Log of Borehole B12	99
6.8	Lithostratigraphic Log for Borehole B2	100
6.9	Cross-section Through Key Boreholes	103
6.10	The location of Key Boreholes	104
6.11	Geology and Fluoride Distribution in the Eastern Part	111
6.12	Fluorosis Map Based on All Water Sources	116
6.13	Fluorosis Map Based on Boreholes Only	117
6.14	Plots of Cations vs. TDS of Water Supplies in the Study Area	128
6.15	Plots of Anions vs. TDS of Water Supplies in the Study Area	129
6.16	Correlations of Na and Cl with TDS in Water Supplies	130
6.17	Distribution of Sodium and TDS in the Study Area	131
6.18	Plots of TDS, Na and Cl Against F	132
6.19	Graphs of TDS vs. Average Concentration of Individual Ions	133
6.20	Plots of Average TDS and ionic concentrations vs. F concentration	138
6.21	Plots of pH vs. F Values in Water Samples	139

### TABLES

3.1	Possible Health Effects of Fluoride	49
4.1	Comparison of Glass and Plastic Sample Containers	54
4.2	The Effects of Al and Fe on FISE Measurements	67
5.1	Fluoride Distribution in the Water Supplies of the Study Area	76



5.2	TDS and Major Ions in Water Supplies of the Study Area	80
5.3	Analytical Results of Bari Salt Samples	82
6.1	Fluoride Concentrations and Surface Geology	85
6.2	Attributes of Selected Boreholes	86
6.3	Fluoride Concentrations in the Lower Karoo	89
6.4	Thickness of Carbonaceous Material and Fluoride Concentration	107
6.5	Ash Content of Typical Coal and Coal of the Study Area	109
6.6	Fluoride Content in the Eastern Part of the Study Area	110
6.7	Key Facilities on the 'All-Water Sources' Fluorosis Map	118
6.8	Key Facilities on the 'Boreholes-only' Map	119
6.9	Comparison of the Two Versions of the Fluorosis Map	120
6.10	Maladies Expected in Each Fluorosis-Risk Zone	124
6.11	Guidelines for Domestic Water Supply Quality	126
6.12	Average Concentrations of Ions vs. TDS Ranges	133
6.13	Average Concentration of Ions Grouped by F Concentration	134

## 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<sup>2</sup> (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.