HYDROGEOCHEMISTRY OF KANO RIVER FROM ITS HEADSTREAM DOWN TO HADEJIA-NGURU WETLAND, NORTH WESTERN NIGERIA

BY

Iliyasu GARBA

PhD/ SCIE/07117/06-07

DEPARTMENT OF GEOLOGY, AHMADU BELLO UNIVERSITY, ZARIA

June2014

HYDROGEOCHEMISTRY OF KANO RIVER FROM ITS HEADSTREAM DOWN TO HADEJIA-NGURU WETLAND, NORTH WESTERN NIGERIA

BY

Iliyasu GARBA

PhD/ SCIE/07117/06-07

A DISSERTATION SUBMITTED TO THE SCHOOL OF POST GRADUATE STUDIES

AHMADU BELLO UNIVERSITY ZARIA, NIGERIA

IN PARTIAL FULFILMENTS FOR THE REQUIREMENTS FOR THE AWARD OF A

DOCTORATE DEGREE IN GEOLOGY

DEPARTMENT OF GEOLOGY

AHMADU BELLO UNIVERSITY, ZARIA

NIGERIA

MAY 2014

DECLARATION

I, Iliyasu Garba with registration number PhD /Scien/07117/06-07 hereby declare that the work in this dissertation titled "Hydrogeochemistry of Kano River from its headstream down to Hadejia - Nguru Wetland, North Western Nigeria has been carried out by me in the Department of Geology. Informationderived from literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma in this or any other institution.

_____ _____

Iliyasu Garba **Date**

CERTIFICATION

This dissertation titled "**Hydrogeochemistry of Kano River from its headstream down to Hadejia – Nguru Wetland, North Western Nigeria**" by **Iliyasu Garba**meets the regulations governing the award of the degree of Doctor of Philosophy (PhD) of Ahmadu Bello University Zaria and is approved for its contribution to knowledge and literary presentation.

_____ _____

Prof.K.Schoeneich
Chairman,
Supervisory Committee

Date

_____ _____

Dr. S.A.Alagbe
Member,
Supervisory Committee

Date

_____ _____

Prof.U. A. Dambatta
Member,
Supervisory Committee

Date

_____ _____

Dr.HaliduHamza
Head, Department of Geology

Date

_____ _____

Prof. A.A. Joshua
Dean,Postgraduate School,
Ahmadu Bello University Zaria

Date

DEDICATION

This work is dedicated to ALMIGHTY ALLAH and my beloved late parents Alhaji Garba Dantsoho and Hajiya Halima Garba Dantsoho

ACKNOWLEDGEMENT

I am particularly grateful to Almighty Allah for giving me the opportunity to start and finish this work. My appreciations also go to my supervisors, Professor K. Schoeneich, Professor U.A.Dambatta and Dr S. A. Alagbefor their meaningful criticisms and supervising the work. Their advice and guidance immensely contributed to the success of this work and its completion. I also wish to express my appreciation to Professor Ibrahim Garba who not only plays the role of a brother but for his encouragement, guidance and counsellorship.

The contribution of my sponsor Kano University of Science and Technology, Wudil will have to be mention in sponsoring me especially in taking the cost of analysing my samples to Poland. In Poland contributions of Dr Eva Kurowska, the Head Department of Fundamental Geology, University of Silesia, Dr, Krystyna, Prof J. Zarba and all staff of the said Department. My special appreciations and thanks go to ABU/University of Silesia linkage under which I did laboratory work and analysis and sponsorship while in Poland.

The contributions of other members of the department especially Dr. Garba Lawan, Dr. H. Hamidu, Dr.A.A. Ibrahim, AuwalYola, Dr.Ismail A. Yusuf, Dr. H. Hamza, S.Magaji, Dr.Najime and Dr. S.A.Arabi for their suggestions in making this work a success their contributions are well acknowledge.

My special regards also to my brothers, Aliyu, Umar, Madani, Murtala, Usaini, Saidu, Abba, Baffa, Ghali, Aminu, Abuhurairah and Abdussalam. My appreciation also goes to my wife HajiyaBinta S.Hamis and my children Halima, Sadik, Aisha, Muhammad and Rabia.

My appreciation also goes to my colleagues, whose names are too numerous to mention, and also to my colleagues in the Department of Geography (KUST) Kano University of Science and Technology, Wudil. May Allah bless all those who contributed in

one-way or the other. My special thanks also goes to DanrakaIsyaku Mustapha my roommate and friend.

ABSTRACT

Hydrogeological and geochemical investigations were carried out to establish level of concentrations of heavy metals and other elements, compounds and species origin from upstream in Kano River down to the Kano metropolis. Concentration levels were measured in groundwater, bedrock and alluvial sediments of the Kano River drainage basin. Ion chromatography, inductively Coupled Plasma Mass Spectrometry (ICPMS), XRF were all used in the analyses of samples collected.

Representative samples of lithological units reveal that some rocks are inherently enriched in heavy metals especially in Co, Cr, Ni, Mn and Zn, relative to their crustal average concentrations. Alluvial sediments especially in the metropolis were also heavily polluted.

Major ions (cations and anions) concentration levels in both surface and groundwater reveals that the water can be used for various uses especially irrigation, domestic and engineering constructions. Based on its organic, inorganic and total carbon contents, the water cannot be used in pharmaceutical industries especially for injections and drugs making. Three major water types were also established: $NaHCO_3$, $CaHCO_3$ and $MgHCO_3$ and the best are the $MgHCO_3$ based on comparison made with Richards (1954).

Water (surface and groundwater) in the metropolis was found to be heavily polluted with heavy metals especially Pb, Cr, Cd, Co, Mn, Zn and As. Consequently the extent to which the pollution has reached downstream was also established and found to have reached most parts of the downstream of the drainage basin, where the water is being used for irrigation as well as domestic purposes. Downstream is an influent river system that is recharged by the polluted water is located. It was established that the pollution especially in the metropolis is caused probably by industries and domestic effluents discharged into the drainage basin.

TABLE OF CONTENTS

Title Page - - - - - - - - - i

Declaration - - - - - - - - - iii

Dedication- - - - - - - - - - - iV

Certification - - - - - - - - - V

Acknowledgement - - - - - - - - Vi

Abstract - - - - - - - - - Viii

Chapter One: INTRODUCTION - - - - - - - - - 1

1.1 Preamble **1**

1.2 Aim of the Study - - - - - - - - 2

1.3 Justification of the Study - - - - - - - - -- - - 3

1.4 Location, Extent and Accessibility - - - - - 3

1.5 Climate and Vegetation - - - - - - - - - - 3

1.6 Drainage - - - - - - - - - 5

1.6.1 Natural Drainage - - - - - - - - - - - - 6

1.6.2 Modified Drainage - - - - - - - 8

Chapter Two: Literature Review **10**

2.1. Geology of the Study Area - - - - - - 10

2.1.1 Basement Complex - - - - - - - 10 (a)

Geology of Kano Metropolis -- - -- 12

(b) Younger Granites - - - - - - - - - - - -15

Geology of Ririwai Ring Complex - - - - - - - 15

2.1.2 Chad Formation - - - - - - - - - 19

2.2 Hydrogeology of the Study Area- - - - - - - - - - 19

2.2.1. Groundwater Distribution in the Basement Complex - - - - - - 22

2.2.2 Groundwater Distribution in the Chad Formation - - - - - - 23

2.3 Heavy Metals as Pollutants of Water - - - - - - - 23

2.3.1 Previous Studies on Heavy Metals Pollution in Kano - - - - - 29

2.3.2 Nigerian Case Studies on Water Pollution - - - - - - - 35

Chapter Three: Materials and Methods - - - - - - - - 42

3.1. Field Work Methods - - - - - - - - - 42

3.2. Laboratory Methods- - - - - - - - - - - - - 45

3.3. Analytical Methods - - - - - - - - - 50

4. Chapter Four: Discussion of Results 51

4.1. Result from Field Measurements-- - - - - 51

4.2. Results from Laboratory Analyses - - - - - - - 51

4.2.1 Heavy Metals in Water - - - - - - - - 51

4.2.1 (a) Heavy Metals in Groundwater - - - - - - 55

Groundwater from Upstream Kano River- - - - - - 56

Groundwater from Midstream Kano River- - - - - - 57

Groundwater from Downstream Kano River- - - - 57

4.2.1 (b) Heavy Metals in Surface Water - - - -- - 63

Surface water from Upstream Kano River - - - - - - 63

Surface water from Midstream Kano River - - - 64

Surface water from Downstream Kano River - - 65

4.3 Comparison of trends in both surface and groundwater - - - - - - - -72

4.4 Comparison of levels of Heavy metals obtained in surface water with standards (EPA, 2004 and WHO, 2011) ---- -- - - - - - - - -- 73

4.5 Comparison of levels of Heavy metals obtained in Groundwater with standards (EPA,2004 and WHO,2011) ---- -- - - - - - - - - - 75

4.5 Major Ions in both Water Samples- - - - - - - 92

4.6 Water Classification - - - - - - - - 94

4.6.1 Classification Based on Major Ions - - - - - - - 94

(a) Piper Diagram. - - - - - - - 94

(b) Schoeller Diagram - - - - - - - - - - - - 94

4.6.2 Water Types of the Studied Area - - - - - -98

4.7 Suitability of Water for Various Uses - -- - - - - 99

4.7.1 Suitability of Water for Drinking and Domestic Use Based on Major Ions and Heavy Metals in the Study Area - - - - - -- 97

4.7 2 Suitability of Water for Irrigation Use Based on Major ions and Heavy Metals in the study Area - - - - - - - - 99

4.7.3 Suitability of Water for Livestock Watering Based on Major ions and Heavy Metals in the Study Area - - - - - 99

4.7.4 Suitability of Water for Engineering Construction - - - - - 101

4.8 Heavy Metals Concentrations in Rocks of the Study Area - - - 101

4.8.1 Preamble - - - - - - - - - - - 101

4.8.2 Chromium - - - - - - - - -102

4.8.3 Cadmium - - - - - - - - - 102

4.8.4 Nickel - - - - - - - - 103

4.8.5 Lead - - - - - - - - 103

4.8.6 Zinc - - - - - - - - - 104

4.8.7 Copper - - - - - - - - 104

4.8.8 Cobalt - - - - - - - - 104

4.8.9 Manganese - - - - - - - - - 105

4.9. Stream Sediments Concentration levelsof heavy metals obtained from Kano River basin - - - - - - - - - - - - - 111

4.10 Evaluation of Organic, Inorganic and Total Carbon in the Surface Water and Groundwater - - - - - - - - - - -119

Chapter Five: Conclusions, Contributions and Recommendations - 123

5.1 Conclusions - - - - - - - - - - - 124

5.2 Contribution to Knowledge - - - - - - 122

5.3 Recommendations - - - - - - - - - 126

LIST OF TABLES

Table 1.1: Some Hydrological Characteristics of River Basins in the Nigerian Savannah - - - - - - - - - - 7

Table 2.1: Average Values in Biotite Granites, Reddened Granite, Greisen Granite and Greisen of Ririwai - - - - - - - - - 18

Table 2.2: Recommended Maximum Concentrations of Trace Elements in Irrigation Water - - - - - - - - - - - - - - - - - 25

Table 2.3: Llimits for Land Application of Effluents - - - - - - - 28

Table 2.4: Upper Limits of Heavy Metals and Boron in Irrigation Water - - 28

Table 2.5: Heavy Metals (mg/kg) in Tannery Sludge Samples - - - - - 30

Table 2.6: Composition of Tannery Sludge in Challawa Industrial Estate -- - -32

Table 4.7: Results of Field Measurements in Boreholes, Hand Dug Wells and Surface Water - 52

Table 4.8: Concentration Levels of Heavy Metals in Groundwater of the Study area - 56

Table 4.9: Concentration levels of Heavy Metals in Surface Water of the Study Area - 64

Table 4.10: Chemical Composition of Groundwater, Upstream of Kano -- 83

Table 4.11: Chemical Composition of Groundwater, Midstream of Kano 84

Table 4.12: Chemical Composition of Groundwater Downstream from Kano Urban Area - 85

Table 4.13: Chemical Composition of Surface Water Upstream of Kano River 86

Table 4.14: Chemical Composition of Surface Water Midstream Kano River - 87

Table 4.15: Chemical Composition of Surface Water Downstream from Kano River - 88

Table 4.16: Summary and Comparison of Studied Parameters in the Studied Water Samples on Heavy Metals with WHO (2011), EPA (2004) and NIS (2007) Guidelines- 89

Table 4.17: Summary and Comparison of Studied Parameters in the Studied Water Samples on Major Ions with WHO (2011), EPA (2004) and NIS (2007) Guidelines - 91

Table 4.18: Sodium Hazard in the study area - - - - - - 96

Table 4.9:Salinity Hazards in the Study Area According to Richard, 1954Classification -- 97

Table 4.20: Heavy Metals Concentrations Levels in Rocks of the Study Area - 106

Table 4.21: Average of Heavy Metals Concentration Levels Obtained from all the Analysed Rocks from Upstream, Midstream and Downstream - - - 108

Table 4.22: Concentration Levels of Heavy Metals in Sediments of Kano River- 111

Table 4.23: Concentrations of Heavy Metals in Sediments from the Study Area with International Guideline of Consensus Based Sediments Quality of Wisconsin. - 112

Table 4.24: Result of Total Carbon, Organic Carbon and Inorganic Carbon Contents in Water from the Kano River Drainage Basin. ---- - - - - - - 118

LIST OF FIGURES

Figure 1: Map of depth of Rainfall in Nigeria Adopted from Schoeneich, et al (1990) - - - - - - - - - - - - - - - 4

Figure 2: Geological Map of Nigeria - - - - - - - - 11

Figure 3. Geological map of Kano Metropolis - - - - - - - 14

Figure 4. Geological Map of Ririwai Ring Complex (After Jacobson, 1977) - 16

Figure 5. Geological Map of the Study Area (After GSN, 2004) - - - 21

Figure 6. Map of Study Area Showing Locations of Sampling Points - - - - 43

Figure 7: Vanadium Concentration inGroundwater from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - - 58

Figure 8: Manganese Concentration in Groundwater from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - - 59

Figure 9: Cobalt Concentration in Groundwater from Upstream Down to Kano and to the Wetland around Turabu - - - - - - - - - - - - - - 59

Figure 10: Nickel Concentration in Groundwater from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - - - 60

Figure 11: Cupper Concentration in Groundwater from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - - - 60

Figure 12: Zinc Concentration in Groundwater from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - - - 61

Figure 13: Arsenic Concentration in Groundwate from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - - - 61

Figure 14: Lead Concentration in Groundwater from Upstream Down to Kano and to the Wetland around Turabu -- - - - - - - - - - - - - - 62

Figure 15: Chromium Concentration in from Groundwater Upstream Down to Kano and to the Wetland around Turabu - - - - - - - - - - - - - 62

Figure 16: Cadmium Concentration in Groundwater from Upstream Down to Kano and to the Wetland around Turabu - - - - - - - - - - - - - 63

Figure 17: Uranium Concentration in Surface Water from Upstream Downto Kano and to the Wetland around Turabu - - - - - - - - - - - - - 63

Figure 18: Vanadium Concentration in Surface Water from Upstream Down to Kano and to the Wetland around Turabu -- - - - - - - - - - - - 67

Figure 19: Manganese Concentration in Surface Water from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - 67

Figure 20. Cobalt Concentration in Surface Water from Upstream Down to Kano and to the Wetland around Turabu - - - - - - - - - - - 68

Figure 21: Nickel Concentration in Surface Water from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - -- - - 68

Figure 22: Cupper Concentration in Surface Water from Upstream Down to Kano and to the Wetland around Turabu - - - - - - - - -- - - 69

Figure 23: Zinc Concentration in Surface Water from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - 69

Figure 24: Arsenic Concentration in Surface Water from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - -- - - 70

Figure 25: Lead Concentration in Surface Water from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - - - 70

Figure 26: Chromium Concentration in Surface Water from Upstream Down to Kano and to the Wetland Around Turabu - - - - - - - - - - 71

Figure 27: Uranium Concentration in Surface Water from Upstream Down to Kano and to the Wetlands Around Turabu - - - - - - - - - - - 71

Figure 28: Map of Concentration Levels of Heavy Metals in Surface Water from Upstream, Midstream and Downstream of Kano River - - - - - - 77

Figure 29: Map of Concentration Levels of Heavy Metals in Ground Water from Upstream, Midstream and Downstream of Kano River - - - - - - 78

Figure 30: Concentration Levels of Heavy Metals in Surface Water Based on EPA2004 - - - - - - - - - - - - - - - - - 79

Figure 31: Concentration Levels of Heavy Metals in Surface Water Based on WHO 2011 - - - - - - - - - - - - - - - - - - 80

Figure 32: Concentration Levels of Heavy Metals in Ground Water Based on EPA2004 - - - - - - - - - - - - - - - - 81

Figure 33: Concentration Levels of Heavy Metals in Ground Water Based on WHO 2011 - - - - - - - - - - - - - - - - 82

Figure 35: Plot of Piper Diagram in the Studied Area (Groundwater and Surface) of the Major Ions and Minor Elements in the Water Sampled - - - - - 93

Figure 36: Plot of Schoeller Diagram in the Studied Area (Groundwater and Surface) of the Major Ions and Minor Elements in the Water Sampled - - - - - 94

Figure 37: Heavy Metals Concentrations in Sediments (Alluvium) of the Kano River Drainage Basin - - - - - - - - - 113

Figure 38: Concentrations of Cr in Alluvium from Upstream to the Downstream of Kano River Drainage Basin - - - - - - 113

Figure 39: Concentrations of Co in Alluvium from Upstream to the Downstream of Kano River Drainage Basin - - - - - -- 114

Figure 40: Concentrations of Ni in Alluvium from Upstream to the Downstream of Kano River Drainage Basin - - - - - -- 114

Figure 41: Concentrations of Pb in Alluvium from Upstream to the Downstream of Kano River Drainage Basin - - - - - -- 115

Figure 42: Concentrations of Cu in Alluvium from Upstream to the Downstream of Kano River Drainage Basin- - - - - -- 115

Figure 43: Concentrations of Zn in Alluvium from Upstream to the Downstream of Kano River Drainage Basin - - - - - - - 116

Figure 44: Concentrations of Mn in Alluvium from Upstream to the Downstream of Kano River Drainage Basin - - - - - -- 116

LIST OF PLATES

Plate1: Effluents Being Used Directly for Irrigated Agriculture in the Kano River Drainage Basin - - - - - - 24

Plate2: Showing the Point of Influx of Effluents from the Tatsawarki River into

Kano River- - - - - - - - 35

Plate3: One of the Strategies by the Industries to Hide Effluent through Piping for a Long Distance Before it empties into Streams in Sharada Area. - - 41

Plate4: Sampled Water Being Filtered with Micro Pore Filter. - - - - 42

Plate 5:Some Water Samples in 200ml Low-density Container - - - - 44

Plate 6: Sampling Surface Water at the Middle of the River Kano - - - 45

Plate 7: The Author in the Laboratory Observing the use of Ion Chromatography Methods of Analysis, Institute of Environmental Engineering in Zabrze, Poland 47

Plate8: Showing the ICPMS Machine Used in Determining Levels of Concentration in Heavy Metals in Institute of Environmental Engineering, Zabrze, Poland.- 48

Plate 9: Laboratory Where Analysis of Samples was done at the Institute of Environmental Engineering in Zabrze, Poland.- - - - - 49

Plate 10: X ray Fluorescence Instrument used in Determining Level of Heavy Metals in Rocks and Sediments in the Institute of Environmental Engineering in Zabrze, Poland - - - - - - - - - - - - - - 50

Plate 11: Battery smelting Industry found in the study area.- - - 55

Plate12:GadarRingim where fishes catch is much done some years back but now this is what fisher get 07/03/12 - - - - - - 72

LIST OF APPENDICES

Appendix I: Results of analysis in determining elemental composition of river sediments and two rocks

Appendix II: Results of Cations, anions and heavy metals in water samples

Appendix III: Results of concentration levels of heavy metals in rocks of the study area

Appendix IV: Results of TOC, IC and TC in water samples

Appendix V: Certification of Fellowship in Poland

Appendix VI: Certificate of Conference Attendance in the course of this research work

Appendix VII: Invitation for a Seminar lecture presented in the course of this research in Poland titled " Environmental Impact of Mining and Industrial development in Kano, north western Nigeria by Garba Iliyasu

LIST OF ABBREVIATIONS

AAS Atomic Absorption Spectrometry

CBSQW Consensus Based Sediments Quality of Wisconsin

CIA Challawa Industrial Area

CIE Challawa Industrial Estate

EC Electrical Conductivity

EXDRF Electron Diffraction X-ray Fluorescence

EPA Environmental Protection Agency

FSN Federal Surveys of Nigeria

ICP-MS Inductively Coupled Plasma Mass Spectrometer

ICP-OES Inductively Coupled Optical Emission Spectrometer

Mg/L Milligram per Litre

Mg/kg Milligram per Kilogram

NIS Nigerian Industrial Standard

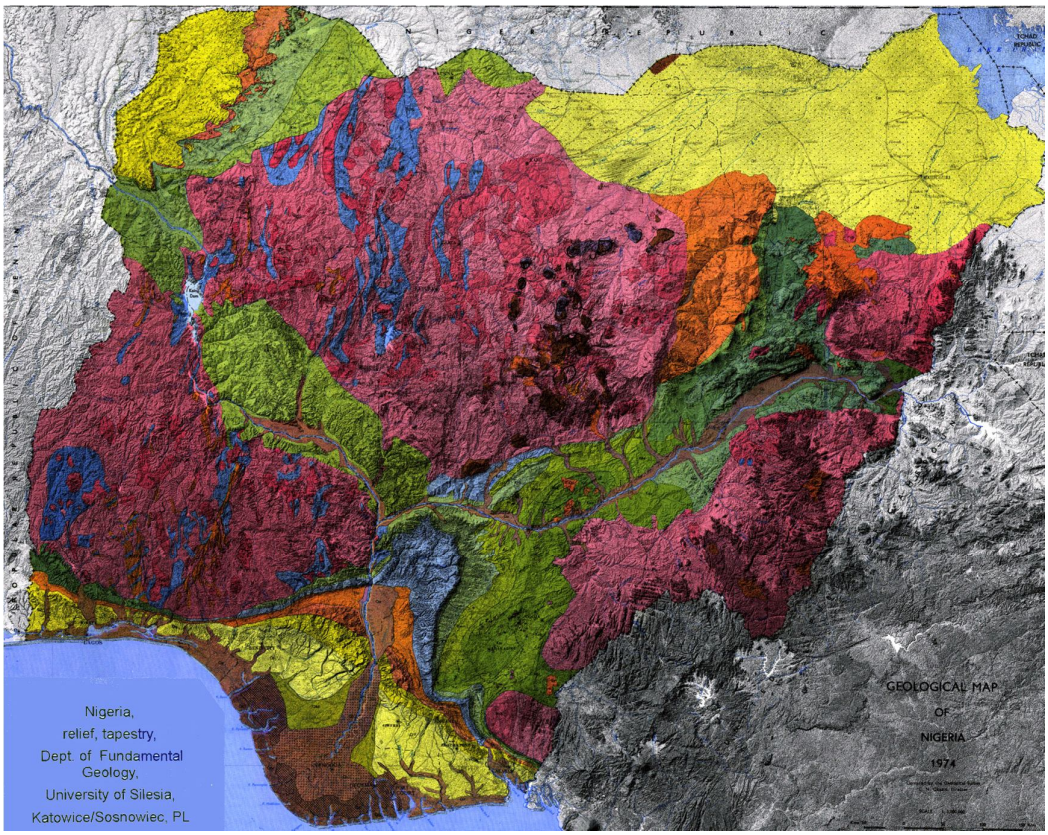
PPM Parts Per Million

PPB Parts Per Billion

PH Hydrogen ion Exponent

TDS Total Dissolved Solids

WHO World Health Organisation


Nigeria,
relief, tapestry,
Dept. of Fundamental Geology,
University of Silesia,
Katowice/Sosnowiec, PL
GEOLOGICAL MAP
OF
NIGERIA
1974

CHAPTER ONE: INTRODUCTION

1.1 PREAMBLE

Studying surface and groundwater pollution is part of protecting water resource and its effect on water quality on health. Under the growing technogenic and anthropogenic pressure water quality study is thenan urgent problem that needs study. In the context of its critical importance, the studies on the distributions and levels of heavy metals in different environmental components like surface water, groundwater, bottom sediments and rocks can never be over emphasised. This kind of investigations allows one to implement environmentally safe and optimal nature management and forecast the state of water resources under the increasing anthropogenic loads. This study will give a key in understanding the nature and rate of anthropogenic action especially by industries in our one of most the important resource after air (water) and that also goes into litho-hydro-biogeochemical cycles. Kano River is one of such an ecological resource of the environment that a study of this type is needed.

Water is a basic resource as well as a necessity for plants, animals and human beings. Wherever demand for safe drinking water has been met, national development and increase in living standards have gone forward; where it has not been met, development has lagged and living standard has remained low. Over the last decades, there has been much interest in the chemical distribution and fate of heavy metals in the environment, including both water and sediments fractions. Significant advance has been made with respect to mining, but in the area of urban water chemical pollution, on which this research focusses its attention, still much remains to be done, especially in areas with adequate land use and improper waste disposal system. Kano metropolis is one of such areas.

The direct dumping and discharge of domestic and industrial wastes into the drainages in the absence of sewage disposal plan causes pollution. To the best knowledge of the author, effluents from industrial and residential areas in Kano are discharged without any treatment to the only perennial rivers flowing through Kano; Kano River and Challawa River. Kano River and its tributary, Challawa River, end in an inland delta known as Hadejia- Nguru Wetland. With its irrigated agriculture, the wetland is the food basket for northern Nigeria. Part of this inland delta (wetlands) is a wildlife refuge. The growing need to preserve and restore the physical, chemical and biological integrity of rivers and other water bodies is implicit in several ongoing studies (Van der Merwe, *et al.,* 1993; Buerman *et al.*, 1995; Don-Pedro *et al.*, 2004).

1.2 Aim of the Study

The research is aimed at carrying out a detailed Hydrogeochemistry of Kano River drainage basin from its headstream up to the Hadejia – Nguru Wetlands with the following objectives:

(a) Producing a detailed geological map of the catchment area (study area).

(b) Determination of heavy metals in representative rocks and water samples for geochemical studies. Heavy elements to be analyzed include cadmium, lead, zinc, copper, chromium, mercury and nickel. Water samples will be taken along the river channel at different locations as well as from hand-dug wells and boreholes along the river channel.

(c) Find concentration levels of heavy metals (Pb, Cd, Zn, Cu, Cr, Co and Ni in groundwater samples taken from both wells and boreholes in and around the river catchment study area.

(d) Find the extent of the pollution from upstream, midstream up to the downstream of the river.

(e) Comparison of these findings with WHO (2011), EPA (2004) standards and NIS (2007) for various forms of uses in the study area.

1.3 Justification of the study

Kano River is probably heavily polluted, 'probably' because analytical researches contradict each other. The writer intends to establish levels of concentrations of heavy metals Cd, Pb, Zn, Cu, Cr, Hg and Ni from the headstream of the river, along the river channel and recognition of possible effect of pollution downstream. The writer also decided to investigates a possible pollution in groundwater within the river catchment and lastly the extent to which anthropogenic factors have impacted the resultant pollution effect (especially industries).

1.4 Locations and Extent

The Kano River catchment is located within Kano and Jigawa States. The river rises from the foot slopes of the Jos Plateau, and flows north and northwest, until about 30 km from its confluence with Challawa River where it sharply swings at about 90^{o} to flow northwards. This is attributed to the topographic divide created by a slight uplift after the Kano valley was formed (Fig. 2). The study area lies within latitudes 10^{o} 30' 52''N to 11^{o} 47' 25''N and longitudes 8^{o} 02'30''E to 8^{o} 45' 40''E. The study area is the same as Kano River Drainage Basin, occupies about 43,285Km^2 approximately 4.9% of Nigeria land mass.

1.5 Climates and Vegetation

The study area falls within the 'AW' climate types according to 'Koppen's' climatic classification with atleast five-month rain and is typical to the northern Sudan Savanna. Climate here is basically of two seasons: wet and dry types. The dry season starts from October to April and usually cool with it harmattan wind carrying tiny dust particles from the

northeast. March and April are usually very hot. The wet season starts in early April to end in September. There is a variation in rainfall distribution in the area and decreasing from south to northeast. Rainfall is accompanied with thunderstorms with their characteristic short sharp rains. The depth of rainfall is contained between 600 mm in the far north and more than 1200 mm in the south (figure 1).

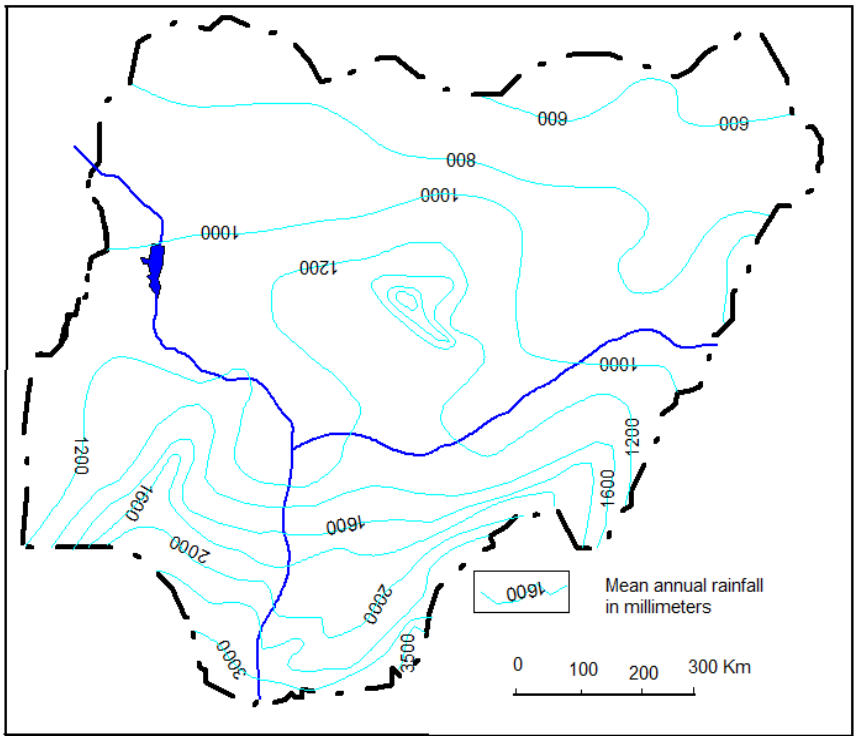


Figure 1: Map of Depth of Rainfall in Nigeria. (After Schoeneich and Amusa (1990)

Vegetation of the study area is a savannah type. The area comprises of both savanna types, the Guinea, at the extreme southern part in Ririwai and Tudun Wada, the Sudan type from Bebeji to Kano area and to the northeastern part somehow Sahel type in Tarabu and Kirikasamma area of Jigawa State.

The reason of these changes is anthropogenic to the extent that the vegetation has largely been cleared for cultivation and fuel and has scattered protected tress with average densities of less than 25 % (Kabiru, 2010). Thickest vegetation is found along the river

channels of Kano River and the floodplains sometimes with impenetrably shrubby vegetation. The surviving woodland is found in the Falgore Game Reserve (370 Km^2) even though it is being degraded due to exploitation, changing into scrubs vegetation or bush made of shrubs and herbs.

Natural vegetation covers less than 5% of the land area except in Falgore forest, which means that most of the indigenous plants species have been extinct, or on their way to it. Few ones are *Adamsoniadigitata*(Kuka), *Vitexdoniana* (dinya), *Doiusyrosmespliformis* (kanya), *Tamarindusindica* (Tsamiya), *Moringaoleifera* (zogale). Others are *ParkiaClapertoniana* (dorawa), which have now declined or getting extinc, *Anogerousleicarpus* (Marke) and *Khyasenegalensis* (Madachi). Most of these are used as fuels and their number are presently under decimation. In the northern parts of the study area, species include Adamsonia digitata (Kuka), *Balirititieasaegytacea* (adua), *A. albida* (Gawo), *Guierrasenegalensis* (Sabara) and *Hypaeni the banka* (Kaba)

1.6 Drainage

The Kano River Drainage Basin is mainly part of the inland drainage system of the Lake Chad Basin. There is considerable relation between rock types and the drainage density in the study area. Highest network of drainage and rivers are found in the Basement Complex areas compared to the Chad Formation in Dambatta, Ajingi and Gaya local governments. The main drainage consists of the headstreams of the river system known as the Yobe in Yobe State, particularly the Kano, Challawa and Gaya Rivers. Both the drainage and the hydrology of the region are influenced by the climate, rock and human activities. Consequently, the discussion of drainage and hydrology here shall be considered under natural and modified varieties.

1.6.1 Natural Drainage

The region drains essentially northeastwards to the Lake Chad, although the headstreams rise from the southeast, south, southwest and west. For example, the Kano River rises from the foot slopes of the Jos Plateau to the south and flows generally north and northwest until about 30 km from its confluence with the Challawa River where it swings more than 90^{o} and flow northeast. The swing is caused by a topographic divide believe to be formed as a result of slight uplift after the Kano valley was formed, diverting the flow of the Kano River from its original probable destination towards the northwest.

Two types of surface drainage can be identified. The principal type is the through-flow, which consists of the Hadejia (known as River Wudil in Wudil) and Jama'are River Systems and drain southeast, south and southwest sections of the region towards the northeast. The important headstreams include the Kano, the Challawa and the Gaya (headstreams of the Hadejia River) as well as, the Bunga, the Katagum and the Fakate (headstreams of the Jama'are). The second type of surface drainage consists of the disappearing flow. This type is made up of individual streams such as the Gari, the Tomas and the Jakara, which drain the northwest and north of the region eastwards. These streams rise and flow freely over the Basement Complex section only to lose their channels, at a short distance east of the Hydrogeological divide into the unconsolidated sediments of the Chad Formation.

The area is divided into two hydrogeological zones, demarcated by a hydrogeological divide. To the west the divide is the zone of high surface water discharge and retention, which coincides with the zone of Basement Complex. In this area volume of groundwater is as much as in the Chad Formation. To the east and north east of the divide is the zone of higher volume than the Basement Complex, which is part of the upper aquifer of the Chad Basin. Retention and flow of water on the surface are very limited in this zone. The first one is characterized by shallow water table and perennial or semi perennial watercourses and all

of them are effluent where as the later, which is the Chad Formation, is characterized by very deep ground water table and only influent flowing from the Crystalline Hydrogeological Province disappearing in the Hadejia – Nguru wetlands. The climate of the region controls the amount of water that is available both on the surface and at sub-surface at any given time within a water-year even though with some factors like geology and anthropogenic in associations. The climate also controls the regime and other characteristics of the rivers. For example, water is abundantly available during the wet months both on the surface and at sub-surface.

The more humid the micro-climatic zone, the more water it had. Thus River Kano, which rises from a fairly humid zone (Ririwai area), has a mean discharge of 39 cubic meters per second (m^3/s) over a similar land area as the River Challawa, which rises from a drier area and has a mean discharge of $22m^3/s$. The streams are characterized by flashy flows, storm discharges and seasonality, except in a few deep ponds and lakes, even on the Basement Complex structure, while groundwater level falls rapidly through seepage, extraction by man and high evapo-transpiration. Table 1.1 illustrates some hydrological characteristics of some savanna river basins before their modification. The conditions presented for the Kano and Jama'are basins relate to the Kano Region.

Table 1.1: Some hydrological characteristics of river basins in the Nigerian Savannah

Basin	**Area Gauged (km^2)**	**Mean Rainfall (mm)**	**Water input (Billion m^3)**	**Discharge (Billion m^3)**	**Estimate ET (Billion m^3)**	**Retained Water (Billion m^3)**
Sokoto	12,590	852	10.73	0.78 (7.3%)	7.08 (66%)	2.87 (26.7%)
Kano	7,097	1000	7.10	1.21 (17%)	4.68 (66%)	1.21 (17%)
Jama'are	7,980	1001	7.99	2.08 (26%)	5.27 (66%)	0.64 (8.08%)

SOURCE: Olofin, *et al.,*(2008)

The quality of water is variable, but it has been found that groundwater, particularly water within sub-surface channel sands, is suitable for human consumption without treatment. Such water is low in total dissolved solids, usually less than 200 parts per million, the solids being of calcium carbonate types. However, untreated surface water is not suitable for human consumption because of the occurrence of water-borne diseases, mostly due to pathogens causing dieses like bilharzias, although it is believed that river-water is good enough for irrigation projects in the area.

1.6.2 Modified drainage

The construction of dams, which started about 1969, marked the beginning of the modification of drainage and hydrology in Kano State. More than thirty earth-dams were planned for the former Kano State,today Kano and Jigawa States and by 1984, about twenty four of these had been completed. The reservoirs of the completed dams and the intricate networks of main distribution and field canals in numerous irrigated sites have created a different type of surface drainage from the ones described above. The modification is great on the Basement Complex section where the dams, reservoirs and canals have been concentrated. Minor, but significant, changes (e.g. perennial flow, flood control) in drainage and hydrology have occurred in parts of the Chad Formation.

In general, the forms of the channels have been affected and the flashy flows and storm discharges have been controlled where dams and reservoirs exist. Water is now available on the surface throughout the year, storm channels are decreasing in width while the Kano River, in particular, has become perennial in regime, and regulated to a mean discharge of 9.6m^3/s downstream of Tiga Dam. Groundwater retention has been improved in the Basement Complex zone in the neighborhoods of the reservoirs. Conversely, groundwater depletion is on the increase in the Chad Formation zone through increased extraction with boreholes and a lower rate of recharge owing to the impoundments upstream.

The quality of water, has not improved. In fact, it is suspected that the quality of groundwater near the reservoirs must have been impaired through mixing with polluted reservoir water. It is known that the concentration of dissolved solids in the water of some of the reservoirs is now high. For example, the water of the Tiga and Bagauda Lakes tastes very salty, particularly during the dry season.

CHAPTER TWO: LITERATURE REVIEW

2.1. Geology of the Study Area

The Basement Complex rocks of Precambrian age are in the western and southern part and southeast part of the study area, which is located in Kano and Jigawa States of Nigeria. The Quaternary Chad Formation dominates the north and northeastern parts of the area. A hydrogeological divide separates the two geologic domains. The basement complex consists of gneiss-migmatite and granites of the Pan-African (600±150 Ma) and older. In the southern tips and southeastern parts, i.e., Ririwai, Fagam, Dutse, Kila-Warji and Birnin Kudu the basement rocks are of the Mesozoic 'Younger Granites' series.

The Geology of the study area will be discussed here under three categories (Figure 3):

Basement Complex (Kano Metropolis) - Midstream

Younger Granites (Ririwai area) - Upstream

Chad formation - Downstream

2.1.1. Basement Complex

Part of the study area, which is located on Basement Complex, has an area of 24,471632,000 m^2 and is underlained by gneiss-migmatite complex, metasediments (schists and quartzites of the schist belts) and granitic rocks of the Older Granites series (Mc Curry, 1973). Minor dykes werefound within these major rocks(Gneisses, migmatites, schists, quartzites e.t.c.). The Basement Complex ranges in age from the Liberian (c. 2,800 Ma) to the Upper Proterozoic (c. 600 Ma). The Older Granites, which intruded the gneiss-migmatite complex and the metasediments (schist belts), consist of porphyritic, medium and fine grained varieties of granites, granodiorites, syenites, diorites and gabbros are mostly products of Upper Proterozoic (Pan-African) event (750-450 Ma). There are also the minor dykes such

as pegmatites, aplites and quartz vein that are either concordant with general strike or cross cut these rocks and are the youngest rocks of the basement complex.

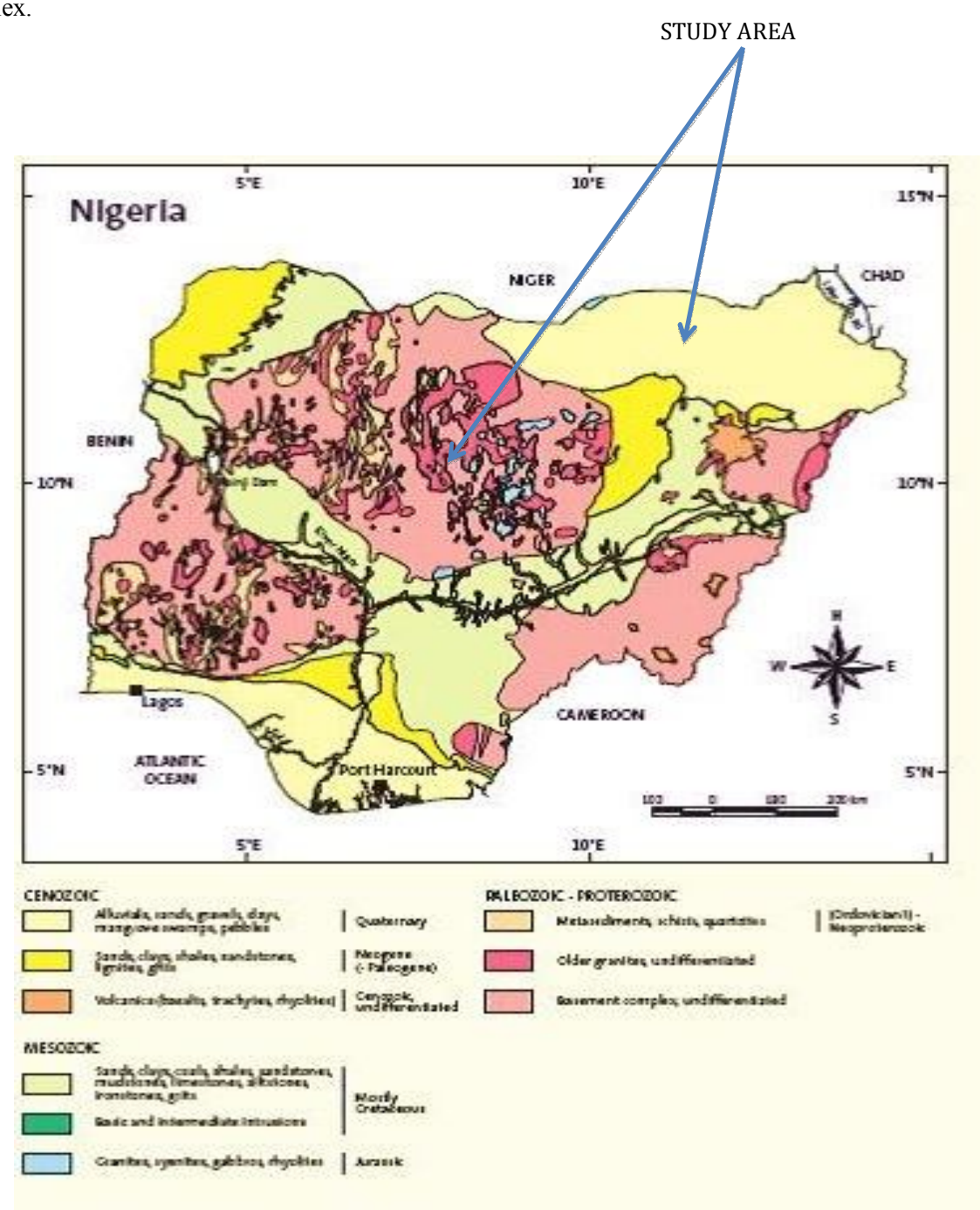


Figure 2. Distribution of rocks in Nigeria after Schluter *et al.*, (2008)

The Mesozoic Younger Granite complexes in the study area are part of the larger anorogenic ring complexes of Nigeria, which are made up of series of volcanic, subvolcanic and plutonic alkaline rocks.

(a) Geology of the Kano Metropolis

The lithological units underlying the Kano Metropolis area, according to Magdi (1999), include the following:

1. Schists

2. Diorites

3. Granodiorites

4. Granites

5. Minor intrusions (pegmatite)

6. Superficial deposits

Magdi (1999) describes the units as follows:

The Schist is fine to medium-grained rocks of argillaceous to arenaceous character, and also usually found in association with diorites boulders. The diorites are dark greenish-grey and medium-fine grained in texture. Their outcrops are rounded to sub rounded boulders, and they both occur in schist and granodiorites.

Granodiorites are porphyritic with phenocrysts of plagioclase often recognized in field outcrops and hand specimen. In thin section, the diorites are made up of mainly plagioclase, biotite, hornblende, pyroxene, olivine and accessory apatite and opaque minerals.

Granites are two types and varied in age, i.e. the porphyritic granites and medium grained granites. The porphyritic are most abundant in colour of pink to light, also white rocky or pink phenocrysts of feldspars is responsible for their variations. Whereas the medium grained granites are equiangular and vary in colour from light to pink. They have are highly jointed covered by laterites found along the valleys of Challawa and Kano Rivers.

Minor intrusive rocks include dykes and veins of aplites, quartz and pegmatites found to be intruding the major rocks.

Superficial deposits result from weathering, erosion and deposition resulting in the formation of products like laterites, alluvial deposits, soils and clays (Fig. 3).

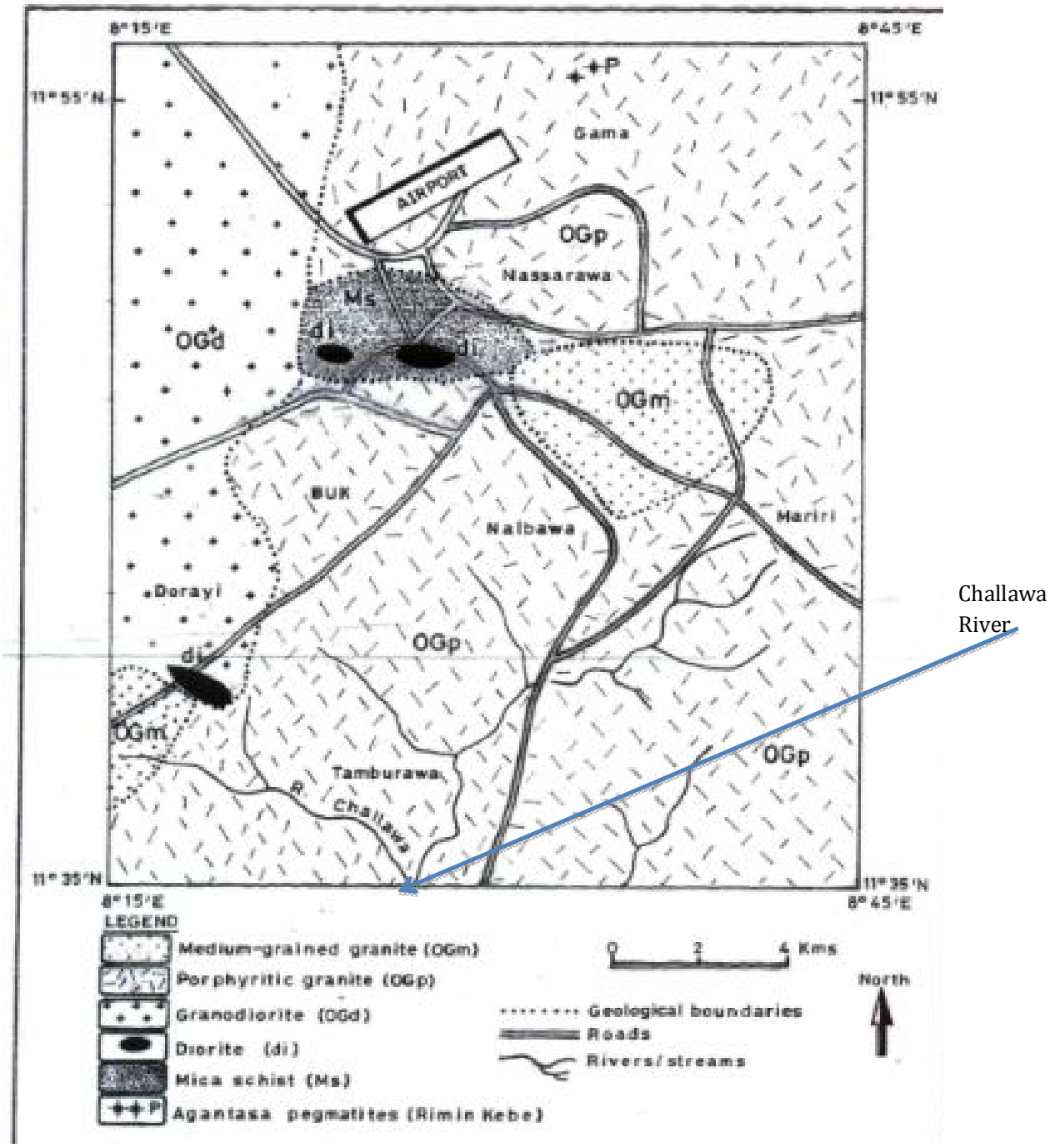


Figure 3. Geological Map of Kano Metropolis (After Magdi,1999)

(b) Younger Granites

The Younger Granites have similarity in the hydrogeological properties with the Precambrian basement complex despite the age difference. The rocks found in these complexes are basalts, rhyolites, tuffs (ignimbrites), afvedsonite-riebeckite granites, syenites, biotite granites and porphyries (as ring dykes). The Ririwai complex is important in this study as it forms the headwaters (upstream) of the Kano River.

Geology of the Ririwai complex

The Ririwai complex has a generally simple pattern consisting of products of initial stage of volcanic activity in form of considerable volume of acid lavas and associated pyroclastics followed by a plutonic cycle where the peripheral ring-dyke of granite-porphyry and central granite plutons of biotite- and riebeckite-granite were emplaced beneath the volcanic pile (Figure 4).

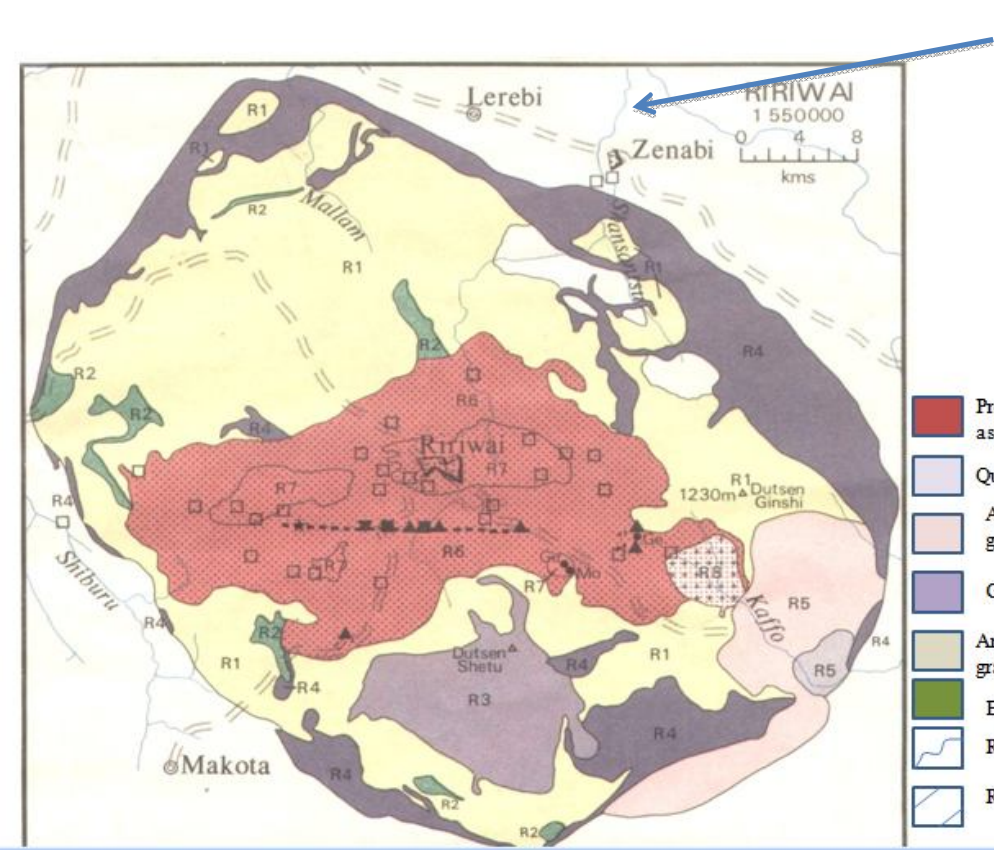


Figure 4. Geological map of Ririwai ring complex (After Jacobsonand Mac Leod 1977).

EXPANATIONS: R1- Pre-caldera agglomerates, ash fall tuffs, crystal-poor ignimbrites and minor comendic ignimbrites. R2 - Basalts. R3 - Quartz porphyry. R4 - Granite. R5 - Aegerine arfvedsonite granite and porphyry. R6 - Biotite granite. R7 - Biotite microgranite. R8 - Arfvedsonite albite granite.

The Basement Complex rocks into which the Ririwai ring complex intruded include gneiss-migmatite and Pan-African granites (Older Granite). The gneisses and migmatites as a group are generally pink/grey and banded, ranging from coarsely mixed gneisses to more diffuse-textured rocks of different sizes. The mineral components are plagioclase, microcline, quartz, biotite and little muscovite. The gneisses include homogenous granite gneisses and a group of heterogeneous gneisses and aplo-pegmatitic granite gneisses. Also the gneisses do not form any appreciable relief being badly exposed and low-lying. They are generally fine to medium grained with occasional fairly lepidoblastic textures. The major minerals are

plagioclase, potash feldspars mainly microcline perthite, quartz and biotite. Accessories minerals are zircon, sphene, iron oxide, garnet, muscovite and sillimanite. The Older Granites occupy slightly more than half of the area and are homogenous than the gneisses. They are both late- and syn-tectonic intrusive granitic bodies. These rocks are all compositionally similar in that they contain quartz, potash feldspars, plagioclase, biotite and sometimes hornblende as the essential minerals in varying amounts. Charkinitic rocks are fine-grained medium grained and locally fairly porphyritic and coarse- grained types. These rocks are also homogenous and unfoliated with joints, outcropping as smooth rounded boulders derived from massive unfoliated rocks by spheroidal weathering.

In Ririwai complex there is substantial output of alluvial cassiterite and columbite concentrates, and tin. The Cassiterite and wolfram are derived from quartz-greisen veins in the biotite-granites, but the columbite occurs as a primary accessory constituent in granite occurring as small acicular prism and platy crystal which seldom exceed 2 mm in length. Also the heavy mineral residues from the biotite-granites contain appreciable amounts of thorite, monazite and zircon. There are also uraniferous pyroclore and is abundant in the albite-riebeckite-granite with small percentage of cryolite. Little beryl has been recorded in the area and genthelvite is also locally abundant in certain tin veins of Ririwai and the genthelvite occurs in several small tin-bearing greisens on the hillside about half a Kmnortheast of Kerigatari(Abaa *et al.,* 1976).

Geochemistry of the rocks in Ririwai based on six samples from biotite granite, the reddened granite, greisens granite and griesen were determined by Abaa, *et al.,* (1976) on both major elements and trace elements. But for this work will focus only on the trace elements.

Trace elements chemistry: Average values determined in the biotite granite, reddened granite, greisenised granite and the greisen are as follow: the main ore-forming elements show increases in the reddened granite: Sn, Cu, Zn, Pb and Lithium, while does not show any appreciable change. These ore-forming elements show a continuous increase from the original biotite granite to the reddened granite to the greisenised granite to the greisens proper where the maximum values are obtained. The increase from biotite granite to greisens is due to the occurrence of the massive ores (casseterite, sphalerite, galena and chalcopyrite), and these are shown on figure 4.

Table 2. 1 Average values in biotite granite, reddened granite, greisenised granite and greisens of Ririwai (After Abaa , (1976)1. Average element content for 6 samples of biotite granite 2. Average element content for 6 samples of reddened granite. 3. Average element content for 6 samples of greisenised granite. 4. Average element content for 6 samples of greisens

Elements (ppm)	**1**	**2**	**3**	**4**
Sn	**17**	**-1740**	**6604**	**24871**
Cu	**4**	**783**	**4773**	**6062**
Zn	**188**	**1804**	**14701**	**21304**
Pb	**29**	**2968**	**16737**	**14400**
Zr	**231**	**314**	**186**	**230**
Li	**338**	**1054**	**2950**	**2987**

2.1.2. Chad Formation

The Chad formation is of lacustrine origin deposited by rivers flowing to the Lake Chad. It is made up of essentially loose sediments consisting of clays, sandy-clays, clayey sands, silts and gravels lying conformably on the Basement Complex. There exist also in small amount of carbonaceous materials (Jones, 1985; du Preez and Richards, 1958).

These clays are whitish, greenish-grey or grey in colour with fine gritty varieties (Isa, 1984). The thickness of the formation does not exceed 152m (du Preez*et al.,* 1958) and are mostly overlain by dune sands alluvium along river channels. There are also longitudinal Seif dunes formed from wind action and are very prominent in the area and mostly consist of fine sands and silts.

2.2 Hydrogeology of the Study Area

It is a known fact that water is the next to air in importance for all living things, particularly for human, plant and animal. Without water there would be no life on this planet known as the Water Planet. Nonetheless, water is never available in sufficient quantity and quality where and when it is required. If it were, all parts of the planet would have been booming with life. Naturally, water is both occurring too much (flood) or too little (drought) and usually in qualities hardly suitable for the intended use. Also, the amount of water that is readily available as freshwater for human, animal and plant use is very small compared with the total amount of water existing on the earth's surface.

The form of water readily available for the use of man and most of the animals and plants is freshwater that accounts for roughly 2.59% of total water, the balance of 97.41% being saline ocean water (WRI, 1988). Regrettably, 76.6% of the freshwater is locked up in ice caps and glaciers that are hardly available, except for a small fraction that melts occasionally. Furthermore, 22.8% of the freshwater is available as groundwater, most of

which is too deep to be exploited easily. Thus, only 0.6% (about 0.014% of total water exists as atmospheric vapour, lake water, soil moisture, river water and water stored in biota. Of this 0.6% of freshwater, the proportion readily available for human development and use is the part found in lakes, rivers and to some extent, in the ground. Indeed, these are the forms on which human existence mainly depends and they constitute the focus of this presentation, even though it is realized that saline water could be (and is being) developed for several other uses as well.

The actual situation and combinations of conditions vary from place to place and the amount of freshwater available is the result of the interactions among a number of factors, two important among which are precipitation and evapotranspiration. For example, some hydrological characteristics of three river basins in the Sudano-Sahelian zone of Nigeria including the Kano Region have already been cited earlier. The average run off from each basin (discharge) contrasts the continental average given by WRI (1988) as 20% of annual rainfall. A common factor of 66% of received rainfall is used for calculating the actual evaporation from the basins in the region.

The discharge and retained water reflect closely the structure of the basins. For example, the area gauged in the Kano Basin is on igneous structure but characterized by very broad alluvial channels. The area gauged in the Jama'are Basin is also on igneous structure but in a slightly more humid zone than the Kano Basin and with a less extensive channel.

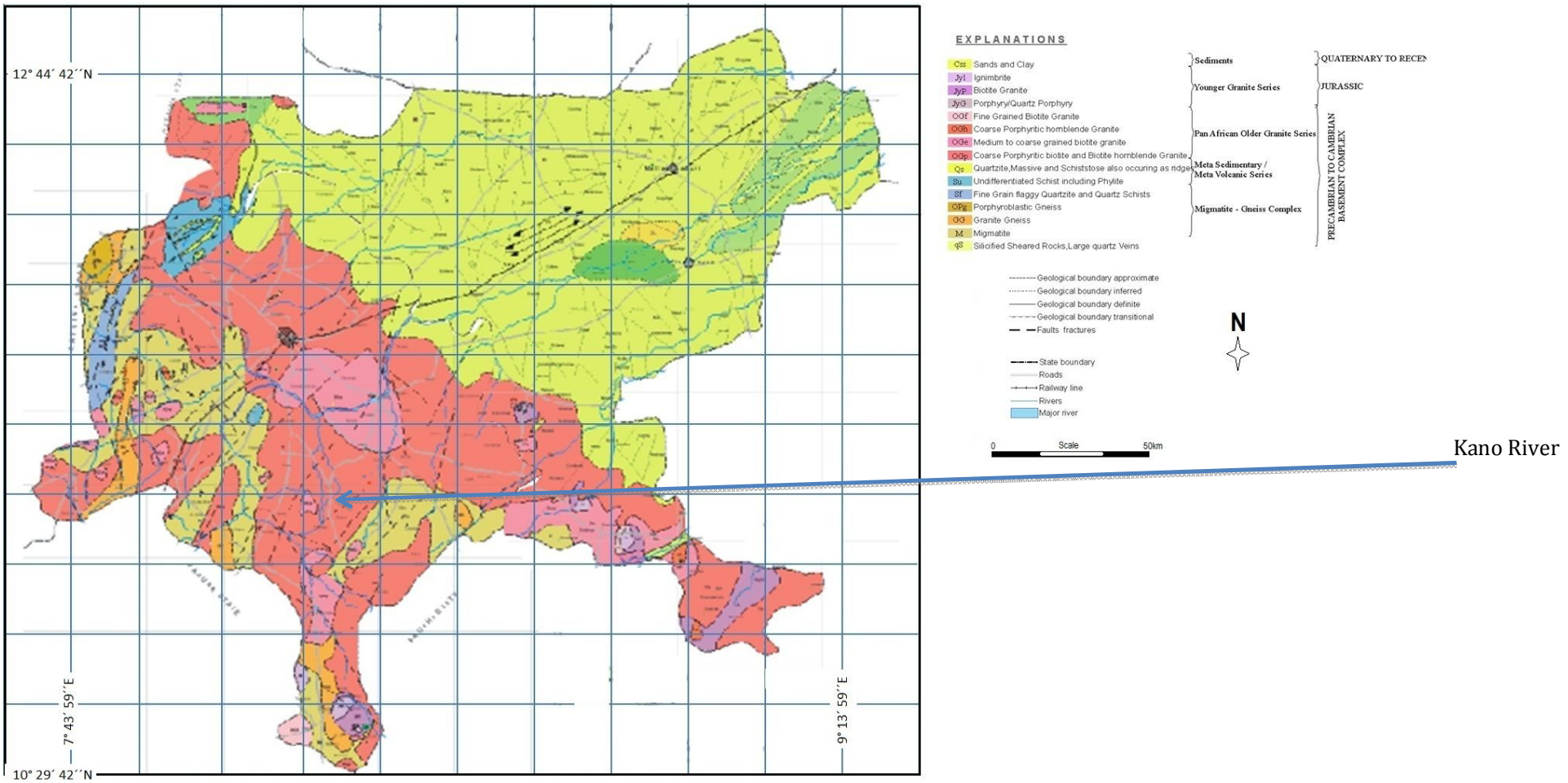


Figure 5. Geological map of the study area

2.2.1 Groundwater distribution in the Basement Complex

While surface water is the more dominant occurrence of water in the Basement Complex area, groundwater predominates in the Chad Formation. Also in the Basement Complex area, sources of groundwater consist of the weathered rock layers (soft overburden), fractured crystalline rock and the alluvial aquifers. The groundwater in the area is of meteoric origin and is controlled by climatic conditions, particularly the nature, duration and amount of rainfall received. Over extraction may result in declining the groundwater and lead to complete depletion of aquifers. It is for these reasons that freshwater are a resource that must be developed and managed in a sustainable manner in the region.

A lot has been done to develop the fresh water resources in the Kano region for both domestic and agricultural uses. There are not less than 22 earth-filled dams located in the Kano Region (Olofin 2000). The reservoirs behind these earth-filled dams were designed principally for irrigation and municipal water supply with flood control and fisheries as subsidiary objectives. For example, the reservoir at Tiga was designed to supply 464.94 million m^3 of water for irrigation and 70.05 million m^3 for urban and rural water supply, besides 149.06 million m^3 in canals and night storages.

The predominance of surface water development through dams and reservoirs behind them in the Basement Complex zone and the predominance of ground water development in the Chad Formation should be noted, while the location of the dams and reservoirs within the region should also be noted. Of course, some boreholes and open wells are established in the Basement Complex area and tapping the fractured crystalline aquifer which is discontinuous with water present in the tectonically fractured zones with poor storage and good permeability. The soft overburden aquifer consists of clays up to 50 m thick with very high storage and poor permeability. The development of groundwater for irrigation and municipal

water supply has received attention where the resource is available all over the region. In ancient times, shallow aquifers were tapped through open wells and ditches to support Shaduf irrigation system on the flood plains of the rivers (Olofin *et al.,* 2008). Today, boreholes, tube wells and wash bores are used to extract groundwater from deep and shallow aquifers respectively under the National Fadama Development Program in the Kano area.

2.2.2 Groundwater Distribution in the Chad Formation

The Chad Formation is today a structure characterized by three levels of aquifer – the upper, the middle and the lower – separated by layers of semi-impervious clayey sediments. The upper aquifer is the least consolidated and is largely a perched type while the middle and lower aquifer is artesian. However, the Chad Formation in Kano State is restricted mainly to the upper aquifer into which surface flow disappears on crossing the Hydrogeological Divide eastwards.

In the Hadejia Valley irrigation Scheme, the project is supported by an artificial reservoir in the Chad Formation. Besides, there are thousands of tube wells and wash bores in the Chad Formation and alluvial complexes in both zones, those in the Chad Formation out-numbering the ones in the Basement Complex zone.

2.3 Heavy Metals as Pollutants of Water

Metals and semi metals listed in the periodic table after calcium cause pollution of water. In water they are present in traces i.e. lessthan one milligram per litre and are often classified as 'trace elements' with other non metallic elements like iodine (I) bromine (Br) and fluoride (F).

There are two groups of heavy metals.To the first one belong mercury (Hg), cadmium (Cd), and lead (Pb). All these three pose danger to health even at a very low level of

concentration. All the three are only in part discharged from the body with products of metabolism and tend to accumulate in the human body. To the second group belong copper (Cu), selenium (Se), antimony (Sb), arsenic (As), nickel (Ni) and vanadium (V). At low concentration, elements from the second group actas micronutrients; only at higher concentrations they become toxic.

Heavy metals do accumulate in the human body like mercury, cadmium or lead (not discharged from human body through metabolism) as is the case with some metals, their solubility is greatest in acid water than alkaline water.After some distance from the source of pollution hydrogen ion exponent increases and so heavy metals tend to precipitate. But then, they accumulate and magnify in alluvium or in cultivated soils(this is the case of irrigation with polluted water). But when hydrogen ion exponent ofwater decreasesthe heavy metals are remobilised and enter again into the water. This is exactly what is happening in the drainage basin especially in Kano metropolis where the effluents are being used for irrigation (plate 1).



Plate 1. Effluents being used directly for irrigated agriculture in the Kano River Drainage Basin

Table 2.2 Recommended maximum concentrations of trace elements in irrigation water: Adopted from Ayers and Westcot (1985)

ELEMENT	RECOMMENDED MAXIMUM CONCENTRATION (Mg/l)	REMARKS
Al	5.0	Can cause non- productivity in acid soils (pH < 5.5). But moreAlkaline soils at pH > 7.0 willprecipitate the ion andEliminate any toxicity.
As	0.10	Toxicity to plants varied widely, ranging from 12 mg/l forSudan grass to less than 0.05 mg/l for rice.
Be	0.10	Toxicity to plants varied widely, from range of 5 mg/l forKale to 0.5 mg/l for bush beans.
Cd	0.01	Toxic to beans, beets and turnips at concentrations as low as0.1 mg/l innutrients solutions. Conservative limits Recommended due to its potential for accumulationinPlants and soils to a concentrations that may be harmful to Humans.
Co	0.05	Toxic to tomato plants at 0.1 mg/l in nutrient solution. Tends to be inactivated by neutral and alkaline soils.
Cr	0.10	Not generally recognized as an essential growth element, Conservativelimits recommendeddue tolack of knowledge on itstoxicity to plants.
Cu	0.20	Toxic to a number of plants at 0.1 to 1.0 mg/l in nutrients solutions
Pb	5.0	Can inhibits plant cell growth at high concentrations.
Ni	0.20	Toxic to a number of plants at 0.5m/l to 1.0 mg/l; reduced toxicityat neutral or alkaline pH.
Zn	2.0	Toxic to many plants at widely varying concentrations; reduced toxicity at pH 6.0 and in fine textured or organic soils.

Cadmium

Recommended level of cadmium concentrationin irrigation water is 0.01mg/l (10ppb), Ayers*et al* (1985) and Schoeneich,(1998) and the later went further to state thatcadmiumis very toxic to beans, and in turn bears its health effects on humansleading to crippling and also results in testicular neurosis and non ovulating in ovaries. According to Wikipedia dictionary (12th December, 2009) inhalation of cadmium containing fumes can initially result in metal fume fever, which may progress, to chemical pneumonitis pulmonary oedema and death. Cadmium is one of the six substances banned by the European Union's restriction on hazardous substances (ROHS) in electronics. Also cadmium and several cadmium containing compounds are known carcinogens and can induce many types of cancer.

Lead

This is another toxic element but does not act as micronutrient even at very low level. It requirement range of concentration in irrigation water should not exceed 5 mg/l (Ayers and Westcot1985;Ewulu, 1983; and Schoeneich, 1998). Schoeneich went further to say that lead could inhibit plant cell growth at very high concentration. Also its effects on human health is said to cause mental retardation in children and its slight deficit causes span and learning abilities in children and in adults results in high blood pressure and kidney problems (EPA, 2000).

Chromium

Mostly chromium is at (Cr^{+6}) and according to WHO (1993) in drinking water is 0.1mg/l (fide:Schoeneich, 1998) i.e. 10ppb Cr^{+6}. Ewulu(1983) in his proposal for water use for irrigation continuously placed it at an average of 5.0mg/l i.e. 5000 ppb. However, it is not generally recognised as an essential growth element. Its conservative limit recommended due to lack of knowledge on its toxicity to plants is 0.10 mg/l(Ayers and Wescot, 1985). Health effect of it on humans is allergic dermatitis (EPA, 2004).

Zinc

Zinc is an essential mineral, necessary for sustaining all life, but at higher concentrations zinc poisoning can occur. It is a key element in prostate gland functioning and reproductive organ growth. In fact it is a co-factor for over 100 enzymes. It has been identified as one of ten major factors contributing to diseases in developing nations like Asia and sub-Saharan Africa. Even though essential for life, its excess in body can be harmful and can suppress copper and iron absorption. It is also a powerful to the point of being corrosive. Stomach acid contains hydrochloric acid in which metallic zinc dissolves readily to give corrosive zinc chloride (Wikipedia encyclopedia, 12th December, 2009).

Levels of zinc in irrigation water is put at **2.6 ppm** accordingto FAO (1985);Ewulu (1983) proposed a table of upper limits of heavy metals in irrigation water use continuously on all soils and for short term use on textural soils and considers 5.0mg/l as upper limit for zinc in water meant for irrigation, whereas, Ayers*et al* (1985) is below 2.0mg/l and went further to state that zinc is toxic to many plants at widely varying concentrations even with the reduced toxicity at pH > 6.0 and in fine textured or organic soils.

Copper

Copper is an essential trace nutrient to all plants and animals life. In animals including humans it is found in the bloodstream as co-factor in various enzymes. However, insufficient amount can be poisonous and even fatal to organisms (Wikipedia 12thDecember 2009)). Its desirable limit for irrigation is 0.2mg/l and toxic to a number of plants at 0.1mg/l in nutrients solutions. Accordingto Ewulu (1983) is 0.2mg/l too, FAO(1985) is also 0.2 mg/l. See tables 3 and 4 for trace elements used in both land and irrigation water according to FAO (1985) and Ewulu (1983).

The table 2.3 below shows limits to which trace elements can be used in land applications as standard by FAO (1985). Whereas, table 2.4 is showing level at which elements in irrigation water can be tolerable in soils.

Table 2.3 Limits for Trace elements in Land Application contained in an min Effluents. (Source: Food and Agricultural Organization, 1985)

Elements	Maximum permissible limit (ppm)
Zn	2.6
Cd	0.2
Cr	0.01
Cu	0.01
B	0.20
N	30
Pb	0.20

Table 2.4. Upper Limits of Heavy Metals to be used for Irrigation Water. (Source: Ewulu, 1983)

ELEMENTS mg/l	For water used continuously in all	For short term (< 20 years) used in textural soils
Cu	0.2	5.0
Cr	5.0	20.0
Pb	5.0	20.0
Zn	5.0	10.0
Mn	2.0	20.0
B	0.75	2.0

2.3.1 Previous Studies on Heavy Metals Pollution of Waters by Industries in Kano

A study conducted in 1995, which monitored the activities of 15 tanneries in Kano, revealed that in all cases, permissible limits for effluents discharged were violated (World Bank, 1995).

Faboya in 1997 noted in Kano, that almost all of the 15 tanneries he monitored violated the permissible limits for effluent with exception of pH and temperature.

Adegoreye (1997) noted that in places like Kano, Kaduna and Lagos, textiles, tanneries, and paint industries discharged their effluents directly into open drainageand water channels.

Another related study by Musa (1997) noted that in Bompai industrial area, liquid waste from the industries in the area are being discharged into the River Getsi mostly through the drains gutters and emptied into the River Getsi. He went further to state that the physical and chemical composition of these industrial effluents varies from one industry to another, and constitutes a threat to the preservation of the quality of the environment and invariably the life of the inhabitants.

Ejechi andOdun (1996) observed the loss of soil fertility, aquatic life and birds' population as a result of commercial and industrial waste deposited in the rivers of Challawa and Kano respectively.

Ahmed and Tanko (1994) have found the concentrations of calcium, magnesium, sodium, manganese, nitrate, chromium and lead varying spatially and seasonally in the rivers of Hadejia of the Kano region. They stated that concentrations of lead, chromium and manganese are in high amount presenting a health hazard and that increasing chemical pollution of water in the study area is due to increasing chemical pollution of water in the area because of the increase in use of chemicals in irrigation and industrial discharges.

TudunWada (2006) observed quality changes in pipe borne water, well water, rivers, air and lands all in Challawa town based onquestionnaires he distributed. Theresults of responses from his disseminated questionnaires werethat 54, 88.1 and 50% of therespondents andhave attributed these changes to pollution effect caused by the tanning industries inthe area. He also went further to report that the state of health from 1999- 2003 ranges from very healthy (57%),not very healthy (18%) and ill (25%) and that there life's pattern of health condition isthe same.

Table 2.5, below shows heavy metals concentrations and pH in the tannery sludge sampled from discharge point of seven tanning industries in Challawaindustrial estatein year 2002 and 2003.In another way in monitoring it was observed that there were changes from 2002-2003 ranges from slight increase (in concentration of zinc and copper) to very slight decrease in nickel, and no change in pH.

Table 2.5. Heavy metals (mg/kg) in tannery sludge samples. (Source: Tudun Wada (2006)

Globus	G L Tannary		Hamahass		Mahaza		Mario		Multitan		Nakudu			
Heavy metals	2002	2003	2002	2003	2002	2003	2002	2003	2002	2003	2002	2003	2002	2003
Zn	2.52	2.75	0.38	0.50	4.38	4.00	2.49	2.52	1.00	3.78	1.13	1.15	15.16	4.20
Fe	6.10	5.53	7.68	7.50	6.73	7.00	8.65	8.60	4.00	3.78	3.07	4.00	13.28	10.07
Cu	2.66	3.00	1.40	1.53	2.52	3.00	1.74	2.05	2.00	2.03	1.72	2.0	2.39	2.50
Pb	1.45	0.92	0.00	0.32	3.07	2.55	1.43	1.0	1.50	1.27	3.48	3.00	1.92	2.00
Mn	3.24	3.55	2.83	2.55	2.85	2.63	4.00	4.00	4.00	3.65	2.15	2.00	2.40	2.50
Cr	4.14	4.25	1.90	1.70	1.67	1.83	070	1.00	1.00	1.02	2.91	2.55	1.39	1.30
Ni	17.8	1.90	0.6	0.65	2.21	2.00	1.49	1.50	1.75	1.64	1.18	2.00	1.72	1.90
Co	1.67	1.50	0.63	0.65	1.90	.00	1.07	1.10	1.50	1.49	1.88	2.00	1.36	1.43

pH	**7.90**	**7.80**	**7.20**	**7.30**	**7.80**	**7.80**	**7.50**	**7.40**	**7.50**	**740**	**7.60**	**7.70**	**7.80**	**7.80**

In Kumbotso area, part of the study area, the Agriculture and Natural Resources Department (1993) has reported the gradual deterioration of RiverTatsawarki (about 2km from Kumbotso) due to continuous discharge of largely untreated tannery effluents. The water quality has become so poor that it could not be used for any purpose; many animals and birds died in the late 80s to early 90s.

Another study by the Federal Ministry of Environment (F.M.E) in 2001 found Cd 0.007; Pb(0.014); Cr, (0.11); Fe, (0.6); Mn 0.01; Ca, (0.0) all inparts per million (ppm) near Kumbotso bridge.

Leewock (1994) in his study on tannery waste from Challawa Industrial Estate (C.I.E.) found out that the sludgecontains total Cu of 32mg/kg; total Mn of 107mg/kg; total Zn325mg/kg;total Fe of 1.85%; total Cr, 10.07%; total Ni of 14.4% and total Pb of 0.92 mg/kg.

Ogbonna *etal.,* (1998) determined the content of tannery sludge samples from Challawa Industrial Estate(C.I.E.), in Kumbotso L.G.A., which is part of the study area. Table2.6shows composition of tannery sludge from the C.I.E. (Challawa Industrial Estate).

Table2.6. Composition of Tannery Sludge in Challawa Industrial Estate: (Source: Ogbonna e*t al* 1998 Fide: Tudun Wada, 2006).

Parameter	S1	S2	S3	F1	F2	F3
pH	8.46	8.35	838	8.62	8.42	9.36
Ash content	44.63	40.93	4595	52.12	39.88	79.67
Losson ignition	55.37	59.07	54.03	47.88	40.12	20.33
Sulphate	2.06	2.31	2.28	1.73	3.61	1.17
Acid insoluble	32.23	14.73	27.21	53.67	45.93	39.59
Mn	0.01	0.04	0.03	0.01	0.01	0.04
Fe	0.47	0.80	0.84	0.09	.0	0.04
Cu	BDL	0.003	0.003	0.002	0004	0.001
Pb	0.03	0.02	0.03	001	0.01	0.04
Cr	1.21	0.69	3.55	0.44	0.45	2.27
Zn	0.13	0.35	0.31	0.01	0.03	0.01
Cd	0.11	0.08	0.21	0.19	0.07	0.09

The major polluter of water is the tannery industries. Processed waste water from these are discharged into receiving rivers without treatment (KNSWB, 2000) and went further to state that there have been of recent a significant effort however to improve effluent situation. The Ministry of Environment has in 1999 promoted an active clean up of industrial plants. All major industries concerned are now legally obliged to provide primary treatment on site prior to discharge to the drainage system (Sequel to this, only two industries in the entire Challawa and Sharada responded to the mandate of the Ministry of Environment as observed during field observation by the Author).

Parkman (2000) reported that there is increased risk of diseases, which could be associated with the unimproved potable water supply, particularly where sanitation facilities lag behind. He also went further to report that domestic and industrial wastewater disposal practices are largely unregulated, resulting in the potential contamination and deterioration of both surface and groundwater quality. He further stated that untreated effluent from tanneries sited in the Challawa Industrial Area obviously concentrated and flows via open ditches from both the Challawa and Sharada Industrial areas. On the Challawa 1A drain (One A drain), much of the effluent is being intercepted in reed lagoons that posses' heavy blankets of sludge and oil type film. Ironically these lagoons are probably serving a useful purpose in that they are preventing some of the effluent from reaching the main river.

Yakubu (2008) observed in Bompai industrial area that though some of the industries engage in some recycling of waste, some wastes especially theuntreated or not properly treated effluents are discharged through drains often and concludes that in the industrial estate available treatment facilities are generally inadequate, poorly maintained and not able to cope with the volume and type of waste generated. He further stated that in the area, river is the most commonly used disposal point having a percentage of 50% of his respondents. He further stated that mean values of V, Cr in the areas were 45.48mg/l instead of NAFDAC(2007) Standard limit of 0.05mg/l and lead of 0.07mg/l of standard 0.01mg/l.

Wastewater from the Bompai Industrial estate is released, without any form of treatment, into the Getsi stream. A significant proportion of the factories in operation at the industrial estate are tanneries and textile mills. Samples of water show high levels of contamination from discharges (Binns *et a*l., 2003). Pollutants such as mercury, chromium, lead and cadmium were found to be in excess of the recommended permissible levels for releases both by industries (Federal Environmental Protection Agency, 1990). Another study

has established that the pollutants have begun to affect the quality of water in shallow hand-dug wells around the Bompai residential areas (Tanko, 1997).

A study conducted on the Salanta stream over the years (Sokoto, 1981, Bichi, 2000, Tanko, 2002) points out that water is highly polluted by the industrial effluents and concludes that the water should not be used for any purpose.

Bala, *et al.,* 2008, stated that industrial effluents discharged into the environment (Kano) pose a threat to agricultural products and health, and in view of this, levels of some heavy metals, such as Zn, Pb, Cr, Cu, Ni, Ag, Fe and Mn show that their mean values (exception of Zn) in water sample analyzed were significantly higher than in the control sit. The study concluded that the values have exceeded the acceptable limits.

Lastly, Tanko (2008) reported that pollution in the Jakara river system results due to industrial activities in the Bompai estate from where effluents are discharged through the Getsi stream into Jakara. In addition to this, heavy contamination is also added to the Jakara through domestic and some (local) industrial waste (around KofarMazugal) from the city. These are drained without any form of treatment to meet the industrial waste in Getsi at a confluence near KwarinDankunkuru.

It is now obvious that heavy metals are being discharged into rivers or water of Kano. Also people in the areastill use the discharged effluents in watering their crops. The soft overburden aquifers in the area may also be affected.Therefore, there is the need to find both effects of the discharged effluents especially heavy metals on both surface and the ground water of the study area. Not only this but also to determine the extent to which the pollution has reached the inland delta of Hadejia- Nguru wetland. Effluents discharge often emptied into the Kano River flowing up to the Hadejia- Nguru wetland. Plate 2 shows the point of influx of effluents from industriesemptied into the Kano River in Mahada (arrow).



Plate 2. Point of Influx of effluents from the Tatsawarki River into Kano River

2.3.2 Nigerian case studies on water pollution

In Nigeria, Faboya (1997) in his work in Lagos noted that Lagos has 60% of Nigeria's industries which generate about 8,500 tonnes of hazardous waste per daywhich are beingdischarged into the environment, with Lagos lagoon taking 10 metric tonnes of BOD (bio oxygen demand) per day whichhas resulted in fishes caught in the lagoon to have high level of lead (Pb), mercury (Hg), and arsenic (A). He also reported that heavy metals from the heavy industries in the Apapa area where the industrial estate contains petrochemicals, detergents, textiles, paper, steel and brewing as well as vehicle workshops, naval ship yards,thermal power plants, and sewage depot; discharging and pumpingheavy metals into surrounding rivers and lagoons.In another related study in Kaduna he also reported that in Kaduna about 160 kilograms per day of heavy metals are discharged in to River Kaduna.

Another study in relation to heavy metals is by Nwanko (1987) who measured concentrations of heavy metals in five streams of the Jos city. He noted that concentration

level of calcium, silver, nickel, chromium and tin in the surface water are much below international average for drinking. In another study in Jos, Schoeneich andAku (1998) found a strong lead pollution of ground water by MakeriSmelting Company, located in southern part of Anglo-Jos industrial estate. They observed that samples taken on 21/03/1999 show 13.174mg/l of lead (Pb) in the water, and concluded that lead, after several years of residence in the soil, is stilll being leached to the groundwater.

Nwanko and Onyeyekha (1989) analyzed water of River Kaduna and found that it was heavily polluted with trace elements emanating from the effluents of the industries in the southern parts of the city.

Khan (1981) noted inAnambra that the state is traversed by anumber of streams, which are tributaries of Niger River and that in the last 10 years the state has experienced a rapid growth of different types of industries e.g textiles, brewery, soft drinks and steel mills. He observed that these industries discharged their industrial waste into the nearest water course as the most convenient method of waste disposal and that resulted in rivers been heavily polluted leading to non-use of the rivers and streams for drinking, recreation and other activities.

Tijjani *et al*. (2004) stated that concentrations of all analyzed heavy metals (Pb, Zn, Cu, Cd, and As) in water phase were slightly higher. He therefore, suggests low to moderate contamination compared to the mean composition of the world. He also state that the contaminations in his studied area are related to anthropogenic sources, mostly from untreated sewage discharge and refuse dumps as well as automobiles emissions and related repair products.

Tukura *et al* (2005) determined the concentrations of trace elements in water samples collected from the AB a reservoir. He determined also the accumulation of these metals (Cd,

Cr, Cu, Pb and Zn) in the gills, livers and muscles and tissues of *Clariasganipenus* and *Tilapia Zillin* in the Ahmadu Bello University dam. Mean levels of Cr (0.68- 0.27), levels in *TillapiaZilli* indicate that Zn and Pb are most available in gills of *Claris Ganepinus*. They indicate P level of 3.10 - 1.6mg/l, and as the most abundant element in water.

Boboye (2008) observed that in Iddah area of southwestern Nigeria, concentrations of Ni and Pb are relatively high at some locations like Ile- Titun, Gege, Adetokun and Oke-Alape. This obviously raises some reservations about the overall quality of the shallow groundwater which might result in cases of cancer, allergies, damage to the central and peripheral nervous system, heart diseases of the immune systems, reproductive disorders and interference with child development.

There exist many studies and related literature on the effect of industrial wastesbeing deposited or disposed into streams in the world over.The major causes of industrial waste in river pollution spring up from the factthat industries dispose off their wastes in a least cost in order to fashionthemselves (Mummy, 1970).Zuidema in 1974 stated that the cause of pollution of rivers originated from heavy pollution from countries upstream and local discharge of waste effluents from purification by industrial plants.

Importance of irrigation water quality standard based on their composition in water was first recognised by Donneen (1949), Hilgard (1960)and lately contributions by FAO in 1985.

Knowledge of the quality of irrigation water is important in assessing its suitability for its use. Degree of adverse effect on soil properties and crop productivity are mainly relatedto the irrigation water irrespective of the nature of the source of the irrigation water (Shamberg, 1978).

Water used for irrigation may contain some heavy metals which are essential to plant growth in trace amounts, namely: zinc, copper, iron, manganese and cobalt while other metals such as aarsenic, cadmium, mercury and lead have not been known to have any function for plants and animals (Greenland and Hayes, 1981). The mere occurrence of these elements, plus certain dissolved salts doesnot render irrigation water unfit for use as the elements may beleached, absorbed, precipitated or fixed, thereby rendering them inactive exceptifit is above the recommended maximum concentrations.

Siddle and Sopper (1976) statedthe concern on the presence of heavy metals in irrigation water, that after years of repeated application to soils in quantities sufficient to supply the plant nutrients needed. The heavy metals added could build upto levels that would be toxic to crops and inturn to animals and man. Evidences also indicate thatcrop plants especially grains are injured before they accumulate.

Ewulu (1983) proposed a table on upper limits of heavy metals in irrigation water and is dependent on the soil type and the length of time the land is going to be irrigated (Table 4). Studies have also shown that the uptake of heavy metals by plants varied according to the amounts applied, soil type and the mode of waste water application (Iskander, 1975). Silty soils tend to retain more metals than sandy soils,while plants grown under spray watering method exhibits higher concentration of metal in the foliage than thosesubjected to flood irrigation (Shainberg, 1978).

Dahiru (1989) used effluents fromAhmadu Bello University waste stabilisation pond for irrigation andtapwater from the Kubanni dam (the dam is serving the University with pipe borne water) as control experiment. Hisresult indicates concentrations of some of the heavy metals: Zn, Mn, Pb and B andconfirms that they are below the permissible limit for irrigation water by FAO standard of 1985. However, considering the concentration of toxic Pb and Cd

in the treated water used in the control experiments, the levels obtained was above the recommended maximum concentrations of 0.07 mg/las against 0.01mg/l,which is an excess of about 0.06 mg/l.Also cadmium on the other hand hasa concentration of 0.01mg/l as against 0.03mg/l. This result therefore indicates invariably that there is pollution by these metals in the dam supplyingdrinking water.

Udoh,*et al.*,(1987) reported the average concentration of Pb in the treated water from the same Kubanni dam as 0.1mg/l,while that of Zn as 1.8mg/l. To solve the long existing controversy, Garba (2000) came up with mean concentration of Pb in the order of <0.24 to <0.01mg/l, proving that there is no Pb pollution within the Kubanni dam. Therefore, results of past workers likeUdoh *et al.*, (1987) and Dahiru(1989) on concentrations of elements, in particular Pb, in the treated water from the dam may not be dwelled upon.

Linda (1974) pointed out the causes of industrial waste river pollution inSwedenwhere large volume of cooling water is discharged into the Gota River. Ironsi (1988)examined the extent of the effect of industrial waste river pollution in the Aral Sea, where he pointed out that in Asia fish catch dropped from 44,000 tonnes to zero in 1950s as a result of pollution of water by toxic wastes which made fish species in the Aral sea to disappear. He went further to state that in 1986, River Rhine was the target of Europe worst ecological accident.

Wardly-Smith(1983) in his work on oil industry pollutionnoted that oil industries are the major sources of river and sea pollution, and this varies from region to region. He also noted that at every stage of transport, refining and use: oil wells can get out of control and release quantities of oil either into rivers, streams or sea. He went to state thatfreshly spills crude oil contains low boiling substances, which are toxic to planktonic organisms.

Klien (1992) observed that salts of heavy metals such as Cu, Zn, Cr in an extremely low concentration from industrial effluents cause damage to plant life and fish.

Kasuya *et al*., (1992) in their study observed pollution by cadmium and lead to have caused the onset of Itai-itai disease, which was as aresult of cadmium that was discharged into the JingzuRiverby a zinc mining industry in the upstream of the Jingzu River in Japan. These effluents were used for irrigation farming in Tayoma plains. They further observed that as the production of zinc in the area increased, the more cadmium is the cadmium being discharged into the JingzuRiver. They continue that this may lead to the increase inthe Itai-Itai disease since still the effluents water is been used for irrigation agriculture in the Tayoma plains.

A report from one of the daily Nigerian newspaper (Daily Trust, 13th February, 2008) captioned 'pollution turns Chinese river red' stated "that heavy industrial pollution has turned a major tributary of China's Yangtse river red and bubbly, forcing a cut in water supplies to some 200,000 people. It went further to report that test on water from Zhejiang River in central Hubei province showed high levels of ammonia, nitrogen, and permanganate, a chemical used in metal cleaning, tanning and bleaching. Report says about 60,000people have turned to using bottled water supplies and limited drinking underground water" (Daily Trust, 29th February, 2008).

Also in the course of the research it was discovered that some industries have defined a way of hiding the effluents by discharging through buried pipes to a far distance before entering into streams of Tatsawarki. This was observed in Sharada Industrial Estate (S.I.E) see plate 3.



Plate 3. A pit containing industrial effluents in pipes before draining into Tatsawarki stream

CHAPTER THREE

3. MATERIALS AND METHODS

The study was done in three phases: field work, laboratory work and statistical analysis of result and interpretation.

3.1 Fieldwork Methods:

Water samples were taken randomly from different parts of the study area from upstream of the river in Ririwai up to the Hadejia-Nguru Wetland ending in Turabu of Kirikasamma Local Government of Jigawa State. Two sample types were taken from both groundwater and surface water as well as from the river channel for two types of analysis, i.e. for major ions and heavy metals.

Wells and boreholes samples were collected with a clean plastic bucket as recommended by Davies (1989). Samples from boreholes were pumped for several minutes with the view that stagnating water within pipes is pumped out in order to sample water coming from the aquifer. Plate 4 shows the author filtering water sample with filter paper.



Plate 4.Water sample being filtered with micro pore filter in the field.

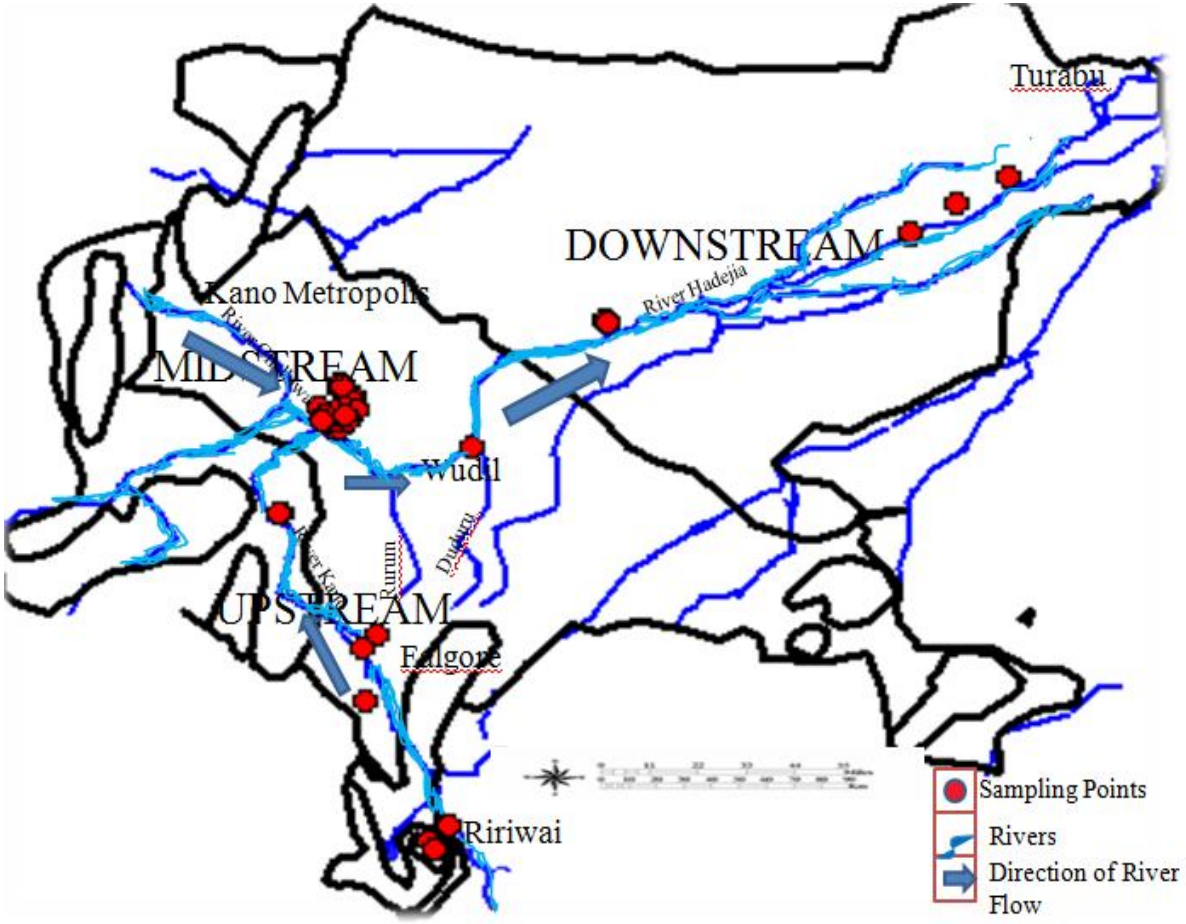


Figure 6. Map of the Study Area (Kano and Jigawa States) Showing Locations of Sampling Points

Plastic bottle containers of 120 ml label were used in taking the samples of water and were rinsed two times with samples before filling it. Also field parameters (Temperature, pH, conductivity and TDS) were instantaneously measured. For trace metals analysis all samples were acidified with drops of concentrated nitric acid to a pH of 2.0, and was tighten and kept in a cooler with ice throughout the period of sampling. Sample bottles were also well labelled (this is shown in plate 5) to indicate those for heavy metals determinations and those for the major ions. Also where samples are from wells depth of wells were recorded in situ and elevations. Also Plate 6 shows that samples of water in river were taken middle of the river



Plate 5. Some water samples in 200 ml low-density container

For the rocks analysis samples from the headstream just to evaluate the background geology from where it flows in Ririwai area for heavy metals only and was concurrently taken with sediments samples within the Kano River from upstream to midstream up to its downstream.

After sampling, all samples were packaged and transported to the Institute of Environmental Engineering Laboratory of the Polish Academy of Science in Zabrze for the determinations of heavy metals in water, sediments and rocks. Ninety water samples were collected for both major ions and minor ions analysis with only two rocks samples from the headstream, 10 for sediments from the three sections of the research area. All samples were collected and delivered to the laboratory within one month of sampling (March 2012).

Another sample of rock was taken after the final presentation of which an observation was made and mandated to a take samples of rocks and analysed them for comparison with level obtained in both surface and groundwater. This was done also and starts from upstream up to the Hedejia - Nguru wetlands 28 rocks samples were taken along the river channel.

3.2 Laboratory Methods

The laboratory method includes determinations of major ions in water using ion chromatography. Ion chromatography also measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulphate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. Concentrations of organic acids can also be measured through ion chromatography. This involves a separation of on Metro- Ohm ion chromatography system (Herisau Metro-Ohm AG, Switzerland) which constitutes of 820IC separation centre, 8181 IC pump, 837 IC Eluent, degasser, 830IC interface, Rheodyne injection valve, metro data 2.3 software and auto sampler (838) advanced sample processor), MSM suppressor and conductivity detector (819 IC).

In the analysis Na_2CO_3, $NaHCO_3$ was used as Eluent preparation and 95% of H_2SO_4 was used as regenerates solution obtained from Fluka (FlukaSteinhen, Switzerland). Standard solutions of inorganic anions were prepared by dissolving suitable salts in water. Analytical

grade of KF, NaCl, $NaNO_2$, $NaNO_3$, K_3PO4, $NaSO_4$, LiCl, NaCl, NH_4Cl, Ca (NO_3), $MgSO_4$ were prepared from Fluka. Water used in the analysis was purified using Millipore equipment and had an electric conductivity of <0.05uS/cm.

Calibrations solutions of the analysed inorganic anions were prepared by diluting the stock standard solution to the required concentrations just before use: Separation conditions are here by listed:

Anions (F^-, Cl^-, $NO2^-$ NO_3^-, $PO_4^{3-}SO_4^{2}$)

Analytical Column- Metrohm Metro Sep A supp 5(250 mm)

Eluent - 3.5 mM $NaCO_3$+1.0mM $NaHCO_3$

Eluent flow rate - 0.7 ml/min

Sample injection volume- 100 ul

Detection - Conductivity with Suppression

Cations (Li^+, Na^+, $NH4^+$, K^+, Mg^+, and Ca^+)

Analytical column- MetrohmMetrosep C4 (250mm)

Eluent -1.7mM, HNO3+, 0.7mM DPA

Eluent flow rate- 0.9 ml/min

Sample injection volume-20ul

Detection- Conductivity without suppression.

Based on this, the results were displayed in computer chromatographs and the flow rate data was extracted and tabulated. Plate 7 below shows author conducting the analysis.



Plate 6. The Author Operating the Analytical Instrument in the Laboratory, Institute of Environmental Engineering in Zabrze, Poland.

For the heavy metals determination in water samples Inductively Coupled Plasma Mass Spectrometry Model 300 was used. This inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometer which is capable of detecting metals and several non-metals at concentrations as low as one part in 1012 (part per trillion). Ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions achieve this. Plate 8 shows the author in front of the ICPMS used in hiswork.

Compared to atomic absorption techniques, ICP-MS has greater speed, precision, and sensitivity. However, analysis by ICP-MS is also more susceptible to trace contaminants from glassware and reagents. In addition, the presence of some ions can interfere with the detection of other ions.

The variety of applications exceeds that of ICP-OES and includes isotopic speciation. Due to possible applications in nuclear technologies, ICP-MS hardware is a subject for special exporting regulations.Also there was the determination of Co, Cd, Zn, Cu, Pb, and Ni in river sediments samples and determination of elemental composition of two rock samples. In the determination of elemental composition of environmental samplesX-ray.



Plate 7. Showing the ICPMS Machine Used in Determining Levels of Concentration in Heavy Metals in Institute of Environmental Engineering, Zabrze, Poland.

For the purposes of determining TOC, use of a high temperature, automated, dry combustion technique after pre-testing and pre-treatment to remove inorganic carbonates. Pre-testing was performed using a 1 to 4 NHCl drop test followed by observation for effervescence to determine if carbonates are present. Alternately, the pH of the sample may be determined and if the pH is below 7.4, then the sample should be free of all carbonates. If carbonates are present, they should be removed using a 2N H_2SO_4 - 5% $FeSO_4$ solution followed by sample drying prior to sample analysis. Combustion of the sample should be at temperatures 135^0C and be performed in a pure oxygen atmosphere to ensure complete combustion of all carbon forms in the sample. Detection of the evolved CO_2 was accomplished using either IR or thermal conductivity detectors (i.e. spectrometric determination). Both detector systems produce comparable and reproducible results.

In the laboratory uncertainties occurs and even during sampling some samples were duplicated (replicates) all taken from same sampled areas concurrently with all in situ measurements. Also calibrations standards were used in calibrating calibrate the analytical equipment. Plate 9 below shows the author in front of the laboratory in Poland.



Plate 8. Laboratory where Analysis of Samples was done at the **Institute of Environmental Engineering in Zabrze, Poland Instytut PodstawInzynierii Srodowiska Polskiej Akademii Nank, Zarbze**

Another analysis of rocks samples was also done in the Department of Geology Kano University of Science and Technology Wudil. DELTA Dynamic XRF (PN103076) was used and heavy metals concentration levels were obtained and a comparison was made with that obtained in both surface and groundwater (Plate 10).



Plate9. X ray Fluorescence used in Determining Concentrations Level of Heavy metals in Rocks and Sediments. Institute of Environmental Engineering in Zabrze, Poland.

3.3 Analytical Method

Results obtained from field and laboratory tests were evaluated using soft wares that produce figures that depict and displays meaningful visual picture of which from which major observations and deductions were made. Soft ware used in the analysis include AQQA Rock ware (a spread sheet used in water analysis(version 1.1.1(1.1.5.1)). Sufer9(Regd.),MapInfo (Regd.), Global Mapper. Data were also treated with theSSP VERSION 16.0 software to evaluate the relationship between the variables and the behaviour of these metals ions in the hydrogeological environments were calculated including the mean, minimum and maximum values with their standard deviations. Water type was also categorised based on its usability

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Result of the Field Measurements

Data obtained from field measurements are for electrical conductivity, total dissolved solids, and elevations of wells, pH and temperature. Results of electrical conductivity ranges from **7 to 59 μS/cm**with an average of **29.5 μS/cm**, while pH ranges from **6.52 to 8.7** and average of **7.17.** Also temperature range of **19.4^{0}C to 54.3^{0}C** and an average of **24.6^{0}C** and elevations of **343 – 880 m** and an average of **472.69 m**. Results of field-measured parameters are presented in the table below (table 4.8).

4.2 Results from Laboratory Analysis

4.2.1 Heavy metals in all water (Both surface and groundwater)

In all the water samples (both surface and groundwater) from the studied area, **V** ranges from 0.09 to 22.78 ppb with an average of 4.81 ppb, Mn ranges from 5.78 to 3693.8 **pp**b and average of 405.98 ppb, Co ranges from 0.11 to 21.24 ppb and average of2.26 ppb,**N**i ranges from 0.26 to 37.01 ppb and average of 7.37 ppb, Cu ranges from 0.17 to 640.93 **ppb** and average of 37.62 ppb, Zn ranges from 15 to 408 ppb and average of 115.03ppb, As ranges from 0.09 to 2.31 ppband average of 0.62ppb, Pb ranges from 0.16 to 834.38 ppb and average of 29.82 ppb , Crranges from 0.16 to 5557.35 **ppb** and average of 419.58 ppb, Cd ranges from 0.04 to 1.64 ppb and average of 0.21 ppb, while **U** ranges from 0.04 to 23.05 ppb and average of 1.75 ppb.

Table 4.8 Results of Field Measurements of Boreholes, Hand Dug Wells and Surface water.

Sample Number, Name of Location and Type Of Sample	Locations	Time	Temp. (^{0}C)	pH	TDS (mg/l)	Elev. (masl)
01. Ririwai BH	10^0 45' 01.3''N 08^0 43 49.2 E	11:10 am	22.4	6.52	010	880
02. Ririwai (SW)	10^0 43' 59.0''N 08^0 44' 41.1''E	12:49pm	23.7	7.28	007	875
03. Zainabi (SW)	10^0 47' 43.2''N 08^0 46'504''E	3:00pm	23.7	7.28	020	616
04. Falgore (BH)	11^0 07'36. 7''N 08^0 34'33. 8''E	8:52am	23.2	6.68	025	589.7
05. Nataala (SW)	11^0 17'47. 4''N 08^0 35'58. 8E	9.45	21.0	7.02	020	517.6
06. Nataala (BH)	11^0 15'45. 4''N 08^0 33'54. 2''E	10:42am	23.3	6.63	019	554.5
07. Ciromawar Kwari (BH)	11^0 37 27.8'''N 08^0 21'58. 7''E	1:00pm	23.5	6.54	011	468.1
08. Chiromawa Kwari (SW)	11^0 37'27. 7''N 08^0 21'39. 4''E	1:25	20.8	7.38	007	459.8
09. Baure (SW)	11^0 50'51. 0''N 08^0 29' 39.2''E	'2:20pm	23	7.42	008	428.4
010. Baure (BH)	11^0 50'46. 1''N 08^0 29 '39.6''E	2:35	23	6.79	008	434.2
011. Majiawa (BH)	12^0 08' 02.8''N 09^0 09'51. 2''E	8:32	22.1	6.93	012	380.3
012. Hadiyau (BH)	12^0 21'40. 4''N 09^0 55'16. 8''E	9; 52am	23.9	6.78	017	357.8
013. Hadiyau (SW)	12^0 21' 55.0''N 09^0 55' 12/1''E	10:05	21.0	7.44	010	346.9

014. Tarabu (SW)	**12^0 30' 40.4''N** **10^0 09'45. 8'E**	**11:20**	**24.2**	**7.67**	**013**	**343.2**
015. Tarabu (BH)	**12^0 30' 42.2''N** **10^0 09'41. 6''E**	**11:32**	**23.7**	**6.78**	**012**	
016. GadarRingim (SW)	**12^0 07' 35.4''N** **08^0 10'07. 5''E**	**8:10**	**19.4**	**7.77**	**008**	**380.3**
017. Hadejia (BH	**12^0 26'30. 9''N** **10^0 01' 59.2''E**	**12:25pm**	**24.0**	**6.78**	**013**	
018. Wudil (SW)	**11^0 47 '56.6''N** **08^0 49'59. 3''E**	**7:59**	**20.0**	**8.70**	**010**	**403**
019. Wudil (BH)	**11^0 47' 56.8''N** **08^0 49' 58.9''E**	**7:15**	**22.5**	**8.50**	**012**	
020. Mahada (SW)	**11^0 50'51. 4''N** **08^0 30' 34.7''E**	**9:00am**	**20.0**	**7.44**	**072**	**427.4**
021. Mahada (SW)	**11^0 50' 43.2''N** **08^0 30' 33.8''E**	**9; 35am**	**20.3**	**8.15**	**008**	**427.2**
022. Magama (SW)	**11^0 52'22. 6''N** **08^0 30'35. 9''E**	**9:43**	**19.4**	**7.51**	**128**	
023. Kaba (BH)	**11^0 52'08. 1''N** **08^0 30'07. 4''E**	**11:00**	**23.3**	**7.32**	**021**	**432.7**
024. Rigafada (BH)	**11^0 54'10. 5''N** **08^0 30' 34.1''E**	**12:20**	**24.2**	**7.23**	**016**	**457.5**
025. Wailari Mosque (HW)	**11^0 55' 06.5''N** **08^0 32'21. 5''E**	**12:45**	**23.2**	**6.73**	**036**	**448.7**
026. Sabuwar Gandu (BH)	**11^0 57'07. 3''N** **08^0 30' 40.4''E**	**1:25pm**	**24.2**	**6.93**	**014**	**472.1**
027. Sharada phase 1(HW)	**11^0 57'47. 8''N** **08^0 30'31. 5''E**	**2; 52**	**23.0**	**6.92**	**066**	**466.7**
028. MaikalwaPri.Sch (BH	**11^0 55' 42.5''N** **08^0 32'42. 5E**	**7:48am**	**22.1**	**7.27**	**070**	**453.0**

029. Wailari (SW)	**11^0 55'25. 1''N 08^0 32' 06.5''E**	**8.15**	**54.3**	**7.05**	**159**	**442.8**
030. Sabuwar Abuja (BH)	**11^0 53' 59.4''N 08^0 27' 24.2''E**	**10:15**	**43.7**	**6.93**	**042**	**461.0**
031.Yandanko (SW)	**11^0 52' 45.9''N 08^0 28'20. 8''E**	**11:00am**	**19.9**	**7.20**	**010**	**434.8**
032. Waratallawa (BH)	**11^0 53'50. 2''N 08^0 32' 54.3''E**	**4:20pm**	**43.1**	**7.08**	**026**	
033. Tanburawa Mosque (BH)	**11^0 52' 14.4''N 08^0 31'54. 3''E**	**4:45pm**	**24.4**	**6.78**	**060**	**462.7**
034. Jan Farms (BH)	**11^0 52' 54.4''N 08^0 31'21. 8''E**	**5:05pm**	**37.6**	**7.45**	**067**	**440.2**
035. RiminZango (BH)	**11^0 52'15. 3''N 08^0 28'05. 3''E**	**10:35am**	**23.4**	**6.56**	**016**	**449.8**
036. SabuwarGandu (SW)	**11^0 57'27. 6N 08^0 30'48. 2''E**	**1:25pm**	**24.2**	**6.93**	**014**	**472.1**



Plate10. Battery Recycling Industrial Plant in the Study Area (11^0 57'47. 8''N - 08^0 30'31. 5''E).

Furthermore, the water samples analysed were grouped on their origin (surface and groundwater). Each group was further subdivided into these from upstream, midstream (Kano metropolis) and then downstream (Hadejia-Nguru wetland). Table 9 below is the results of concentrations obtained in groundwater in both upstream, midstream and downstream of the study area.

(a) Heavy Metals in Groundwater

The results of geochemical analysis of heavy metals in groundwater samples from the upstream midstream and downstream of Kano river were statistically analyzed. The range and mean are tabulated below

Table 4.9 Concentrations levels of heavy metals in groundwater

Elements	Upstream		Midstream		Downstream	
	Concentrations in ppb		Concentrations in ppb		Concentrations in ppb	
	Range	Mean	Range	Mean	Range	Mean
V	0.63 - 6.73	3.13	0.44 - 6.72	1.77	0.64 - 20.48	9.20
Mn	5.78 - 2922.2	679.03	13.05 - 513.09	112.75	13.05 - 513.09	634.79
Co	0.11 - 5.21	1.34	0.16 - 1.82	0.61	0.6 - 21.24	5.20
Ni	2.03 - 21.86	6.62	2.75 - 9.15	5.50	2.29 - 37.09	11.47
Cu	1.86 - 25.49	7.96	5.27 - 64.95	23.03	3.32 - 640.93	137.55
Zn	50 – 393	132	52 – 408	153.45	15 – 124	75.2

As	0.09 - 0.39	0.25	0.09 - 1.58	0.47	0.09 - 2.27	0.64
Pb	1.8 - 30.04	7.69	2.62 - 834.38	80.63	2.18 - 42.69	12.91
Cr	2.26 - 4.59	3.58	2.86 - 16.4	7.41	1.83 - 80.18	42.51
Cd	0.33 - 1.64	0.63	0.04 - 0.09	0.05	4.73 - 192.69	48.43
U	0.051 - 3.98	0.91	0.07 - 23.05	2.77	0.31 - 3.87	1.40

Groundwater from upstream Kano River

From Table 4.9, it can be said that the water from the upstream side of the Kano river is contaminated and can be taken as background samples taken in the upstream sides, only one (sample in Table 4.13) has a higher concentration of heavy metals. This may be related to the geology of the area where the sample was taken from. The high Pb concentration in the said water sample may be from PbS (galena), which occurs outcropping in the sampled area. The mechanism through which the Pb goes into the groundwater in this area is by the activities of weathering, leaching, infiltration and recharge usually under the influence of gravity and then mining). There is also high concentration of Mn in the same sample and may also be related to the geology of the area and mechanism by which it goes into the water of this section is envisaged to be by precipitation and absorbance of free air in water which gives a brown coloration and settles down. The source of Mn source may be related to that of iron (Fe) contents in the rock, which is mostly enriched. Mn and Fe occurs together in rocks of this section because of their geochemical similarities (primary origin in rock), dispersion and secondary dispersion through weathering taking them into water

Groundwater from Midstream Groundwater (Urban Kano Area)

Eleven samples were taken in the midstream and analyzed and the results obtained shows that five of the eleven have higher concentrations higher than the standards. The metals are As, Cr, Pb, U, Co, Ni, Mn and V. The mechanism through which theses metals go into water is mainly dispersion (leaching, infiltration and recharge). The most important here are Cr, Pb, and As. These are sourced from industries discharge their effluents into Kano and Challawa rivers. However, some of the elements are dispersed through secondary type processes like weathering of the rocks in this section.

Groundwater Downstream Kano River

In the downstream sides only two samples show high contaminations by these metals i.e. Mn, Ni, Cu, Zn, Pb and Cr. Sample 183 shows that the concentrations of all these metals were above standards, and it was taken from a borehole at the last point sampling point located in the wetland, where the river turns into an influent one. The sample is also from a borehole and levels were above the standards especially for domestic use and for drinking. Pb may be from scree or sourced from primary dispersion (inherent) and secondary (weathering, erosion and then deposition) of rocks in this section. The concentrations of heavy metals in groundwater from the upstream of Kano river drainage to the downstream point around Hadejia -Nguru wetland, are graphically shown in bar charts of Figure 7-17

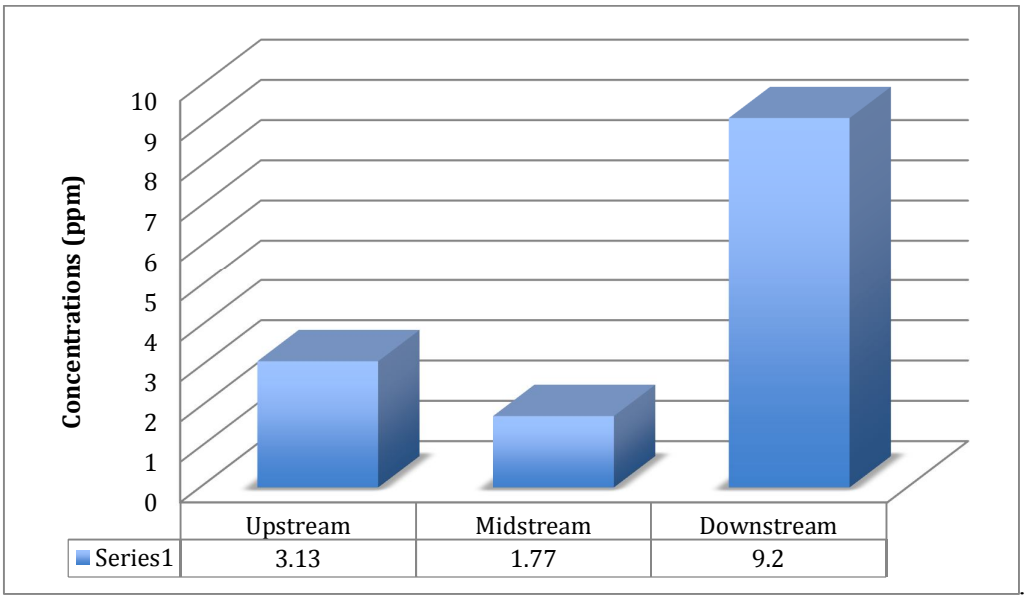


Figure 7. Vanadium concentration in groundwater from Upstream to the Downstream of Kano River

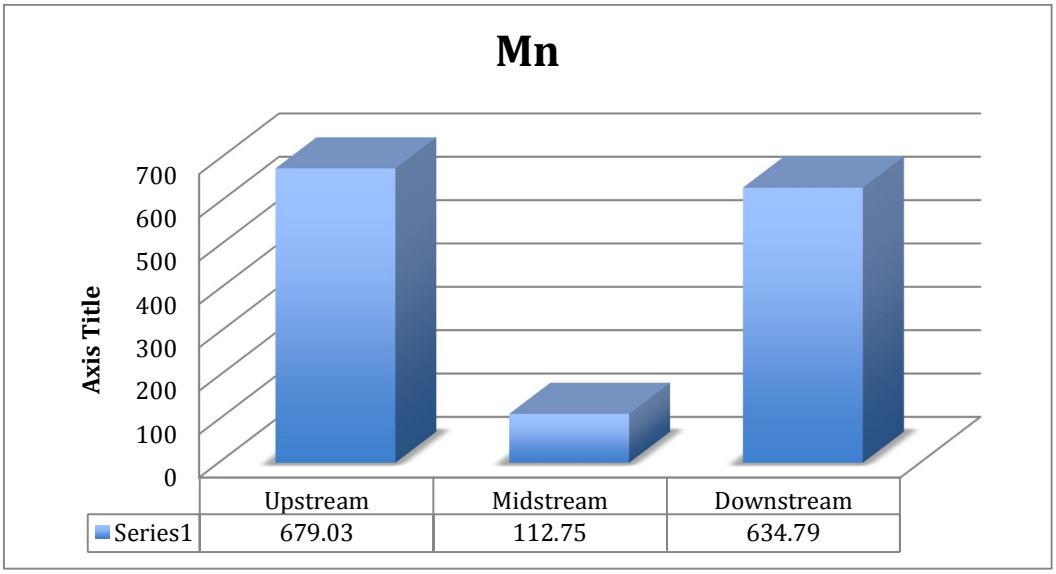


Figure 8. Manganese concentration in groundwater from upstream to the downstream of Kano River

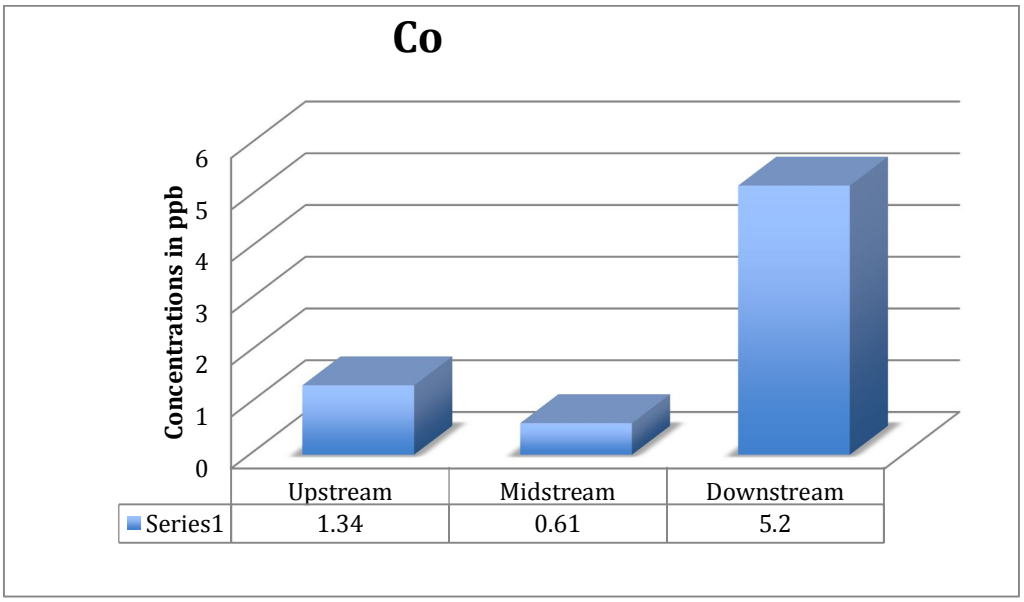


Figure 9. Cobalt concentrations in groundwater from upstream to the downstream of Kano River

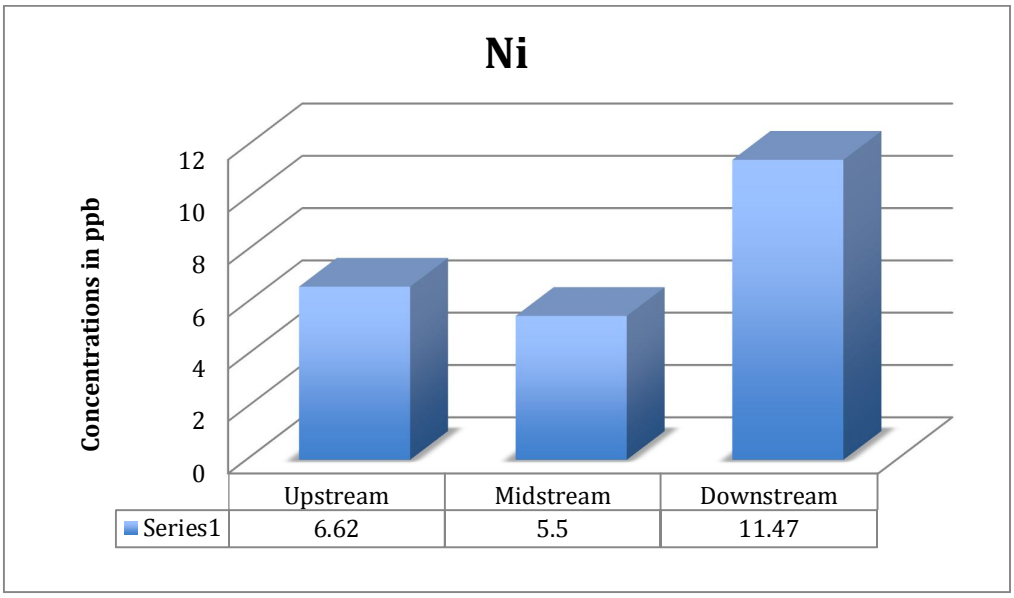


Figure 10. Nickel concentrations in groundwater from upstream to the downstream of Kano River

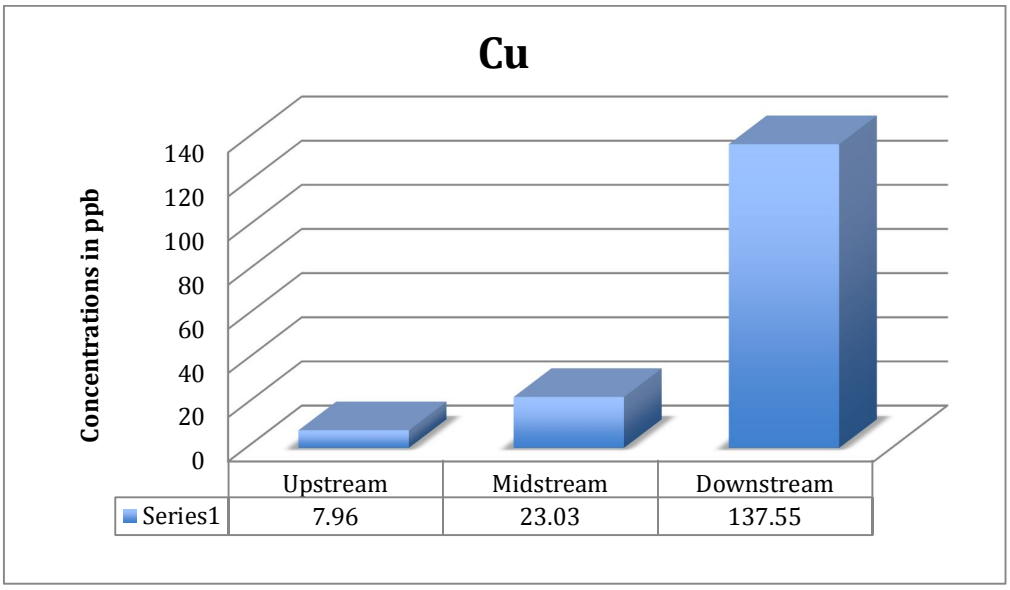


Figure 11. Copper concentrations in groundwater from upstream to the downstream of Kano River

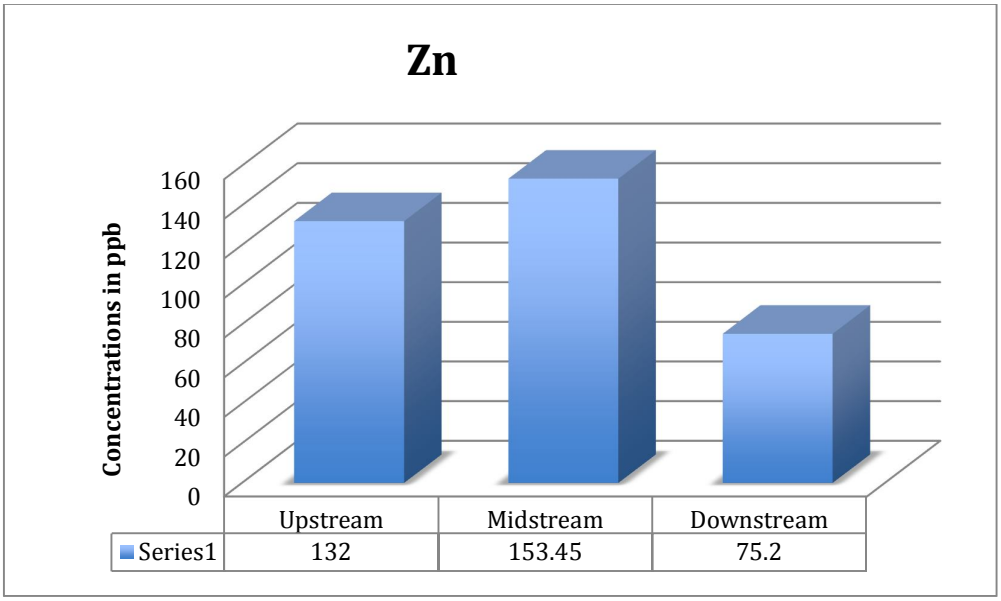


Figure 12. Zinc concentrations in groundwater from upstream to the downstream of Kano River

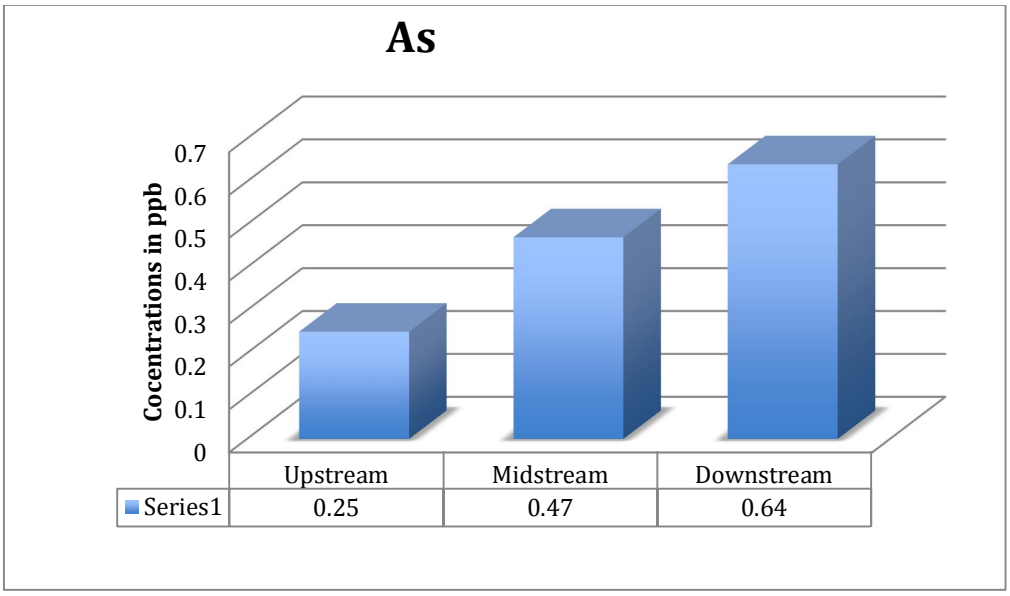


Figure 13. Arsenic concentrations in groundwater from upstream to the downstream of Kano River

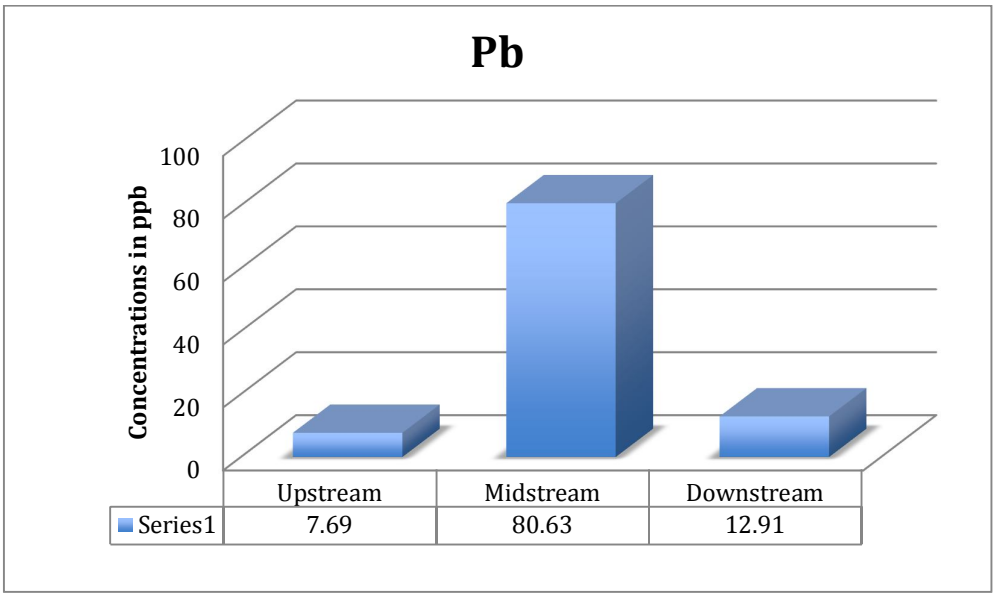


Figure 14. Lead (Pb) concentrations in groundwater from upstream to the downstream of Kano River

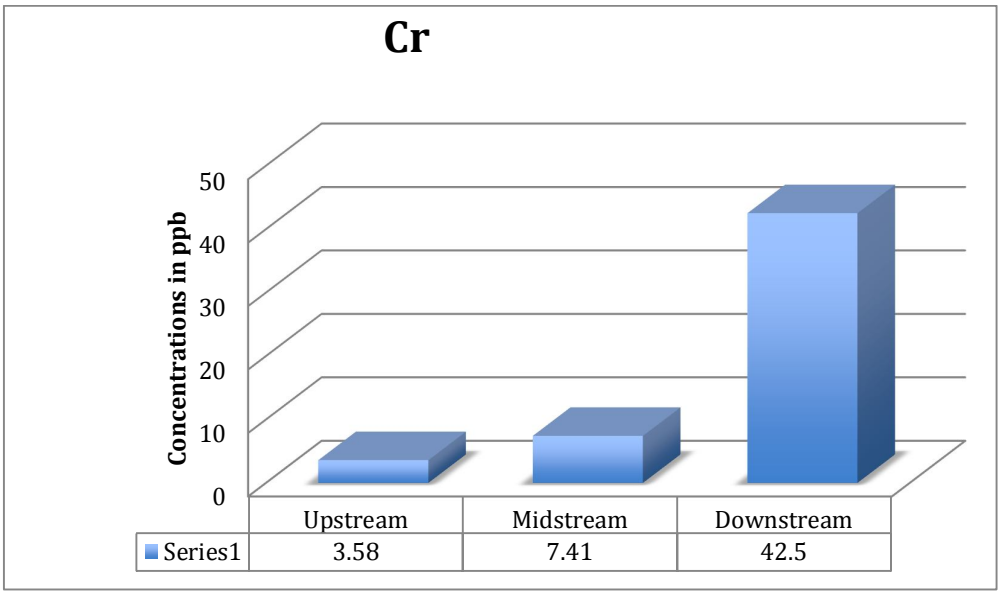


Figure 15. Chromium Concentrations in groundwater from upstream to the downstream of Kano River.

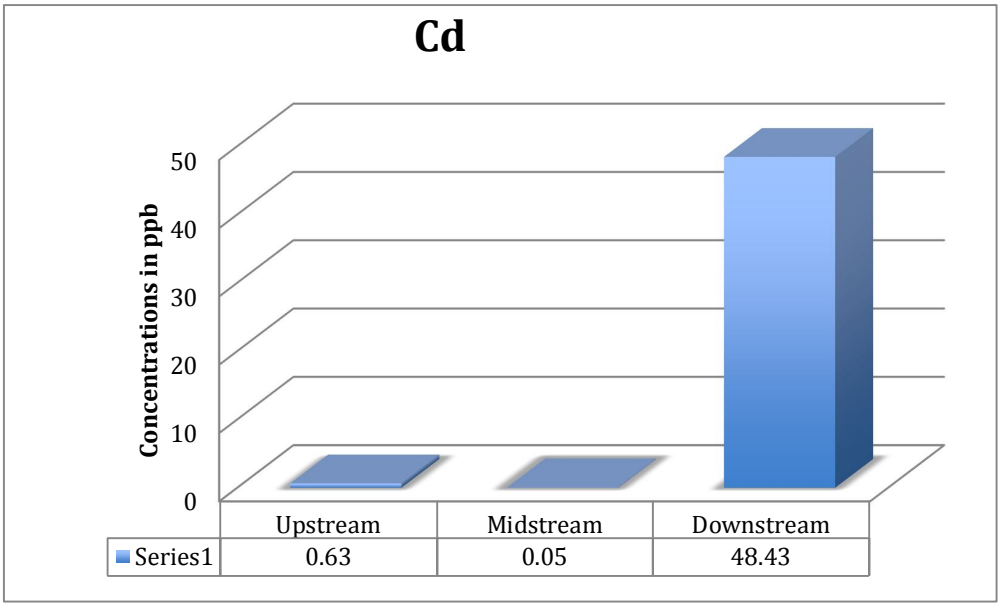


Figure 16. Cadmium Concentrations in groundwater from upstream to the downstream of Kano River

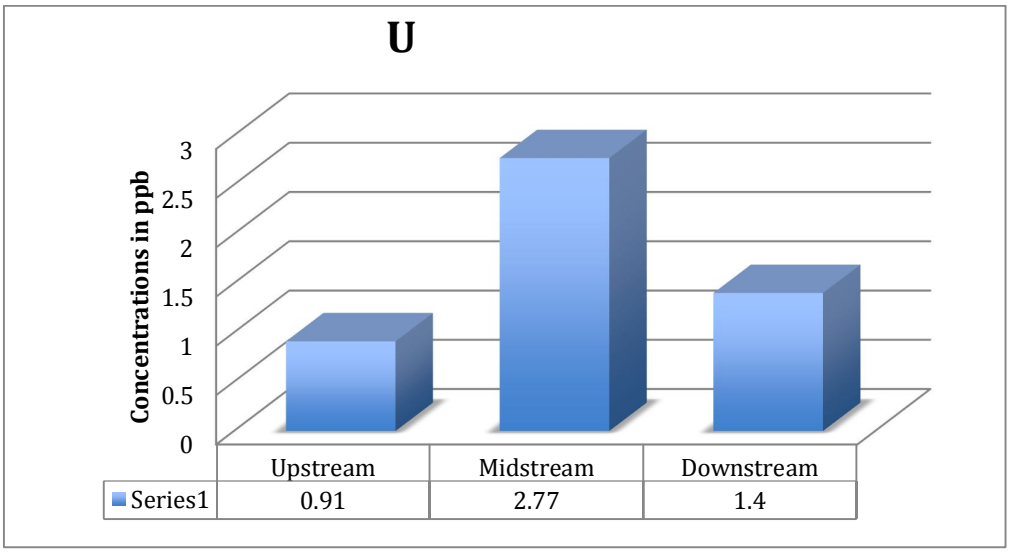


Figure 17. Uranium concentrations in groundwater from upstream to the downstream of Kano River

(b) **Heavy Metals in Surface water**

The results of geochemical analysis of heavy metals in groundwater samples from the upstream midstream and downstream of Kano river were statistically analyzed. The range and mean are tabulated below.

Table 4.10. Concentrations levels of heavy metals in surface water

Elements	Upstream Concentrations in ppb		Midstream Concentrations in ppb		Downstream Concentrations in ppb	
	Range	Mean	Range	Mean	Range	Mean
V	0.39 – 7.51	3.36	7.89 - 22.7	11.89	0.09 – 6.03	1.56
Mn	41.5 -3 693.8	813.79	51.56 - 477.48	250.13	36.91 – 575.43	242.41
Co	0.14 – 9.7	2.43	1.41 – 5.39	3.87	0.25 – 1.93	1.23

Ni	2.17 – 4.76	3.01	5.35 – 22.76	13.98	0.26 – 4.59	2.89
Cu	1.79 - 4.83	2.80	6.02 – 113.38	55.89	0.17 – 7.17	3.6
Zn	32 - 95	55.6	59 - 242	117	62 - 118	88
As	0.24 – 0.36	0.31	0.12 – 2.31	1.26	0.33 – 0.67	0.52
Pb	2.3 – 6.17	3.44	3.93 – 17.69	10.19	0.16 – 5.13	2.41
Cr	2.69 – 3.69	3.27	61.38 – 5557.4	2353.7	0.16 – 30.88	9.08
Cd	0.09 – 0.54	0.24	0.04 – 0.61	0.14	0.04 – 0.08	0.06
U	1.19 – 1.44	0.56	0.97 – 4.44	2.68	0.04 – 0.54	0.22

Surface water from upstream River Kano

Here concentrations obtained in samples were within the standard averages. Only one sample was above the standard levels. The compositions of Co, Mn, Ni, and U in the sample are higher than the standards levels and this is from Ririwai, which is a mining area. Mechanism of dispersion may be mainly primary (genetic included groundwater/ surface water interractions,) the secondary and then tertiary dispersion by human (mining).

Surface water from midstream Kano River (Kano metropolis)

The water in this section is contaminated with heavy metals. Concentrations obtained from all samples within the metropolis were high and above standards levels. Table 4.15 shows metals concentrations in the sections. Those that was higher than the standard Cr, Ni, Cu, U, As, Pb. It has been observed that samples from midstream are contaminated with these metals based on concentrations levels. The mechanisms of dispersion are mainly industrial of

which effluents from industries are discharged into the Tatsawarki stream including household's wastes. These effluents then empty into the Challawa River and the Kano River. It is important to not here that Kano metropolis got its drinking water supply through the tube well constructed in the drainage section of the midstream where the effluents are concentrated. The Tamburawa water works is few kilometers from the point of influx of of these influents into the river. It is the same water that flows to the Hadejia- Nguru wetland upto Tarabu. It is the same water that was dammed downstream in Marke and Miga. These transported and dissolved metal may settle in these dams and on top of Sediments may be a mixed up in water by cattle's or humans and may flow out through their spillways downstream.

Sediment analysis also shows higher concentrations of heavy metals in the midstream. The sediments serve as filters in infiltration of water into the ground, but since they contain these metals it means water passes through the sediments with out any absorbance. Surface water the same results obtained in the surface shows the relationship between surface and groundwater.

Downstream Kano River

The concentration of Cr, Zn and Mn determined in this section are above standards. Cr contents in the water may probably be the reason for the drop in fishing activities in downstream areas. This made fisher men to migrate to other forms of economic activities. Personal interview conducted in the course of this research work with fisher men shows that they all believed that industrial effluent discharged from Kano industries is responsible for killing fishes in the river and they blame the tanneries and they claim that the effluents are seasonal. The effluents rich water is called "Ruwan Jima" meaning dissolved tannery waste.

Similarly the concentrations of heavy metals in the analyzed surface water samples fro upstream to the downstream site of the kano River in the study area are displayed as bar charts in Figures 18-28. These include V, Zn, AS, Cr, Cd, Ni, Co and U.

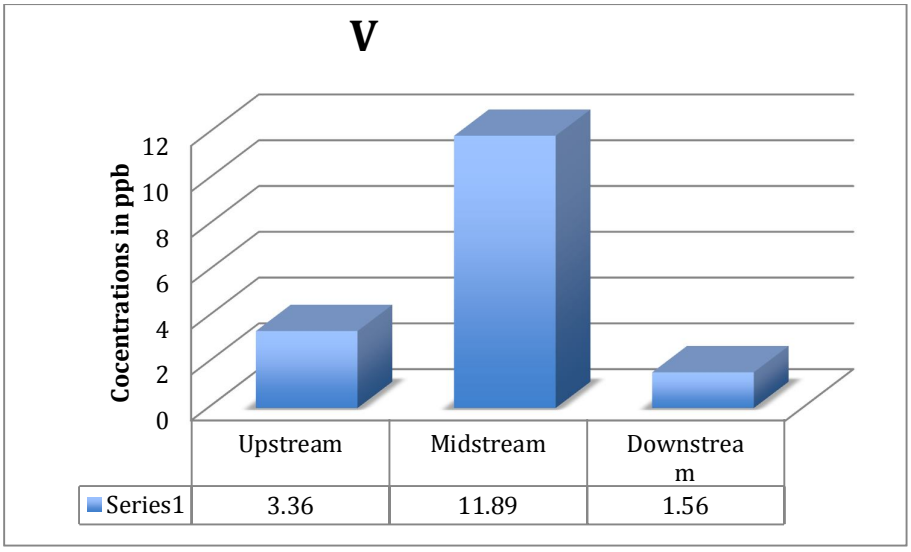


Figure 18. Vanadium concentrations in surface water from upstream to the downstream of Kano River

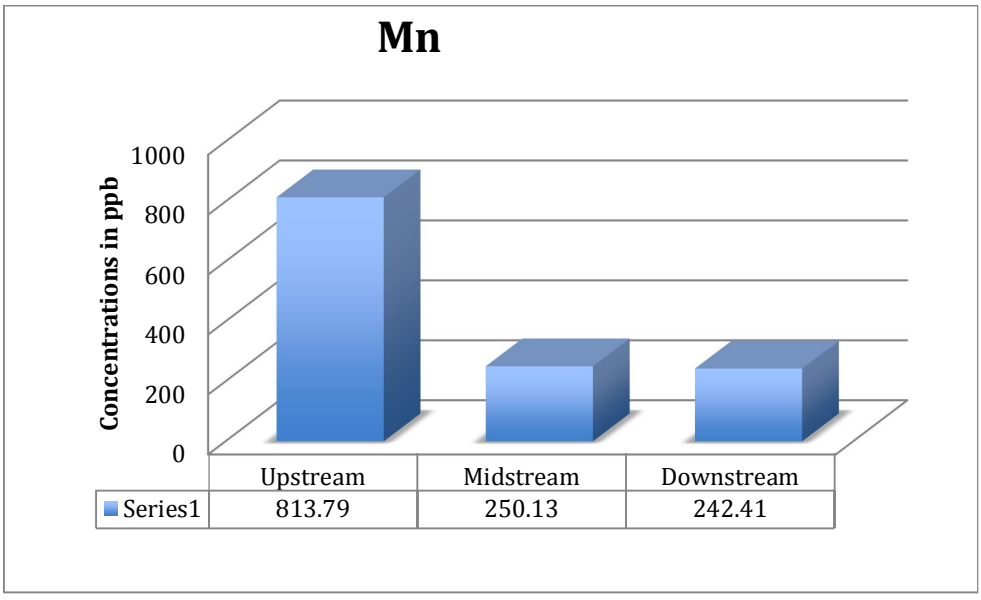


Figure 19. Manganese concentrations in surface water from upstream to the downstream of Kano River

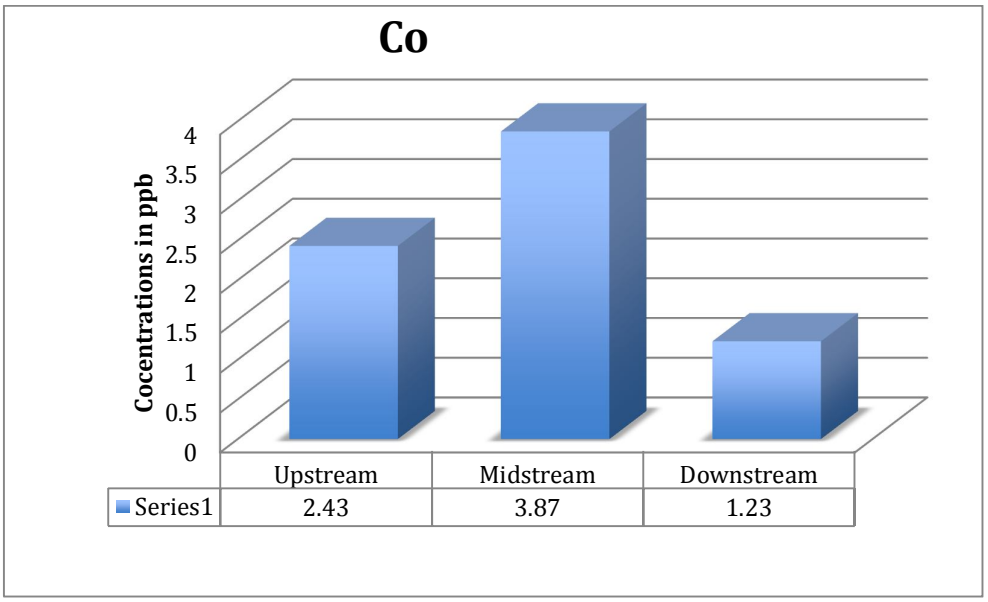


Figure 20. Cobalt concentrations in surface water from upstream to the downstream of Kano River

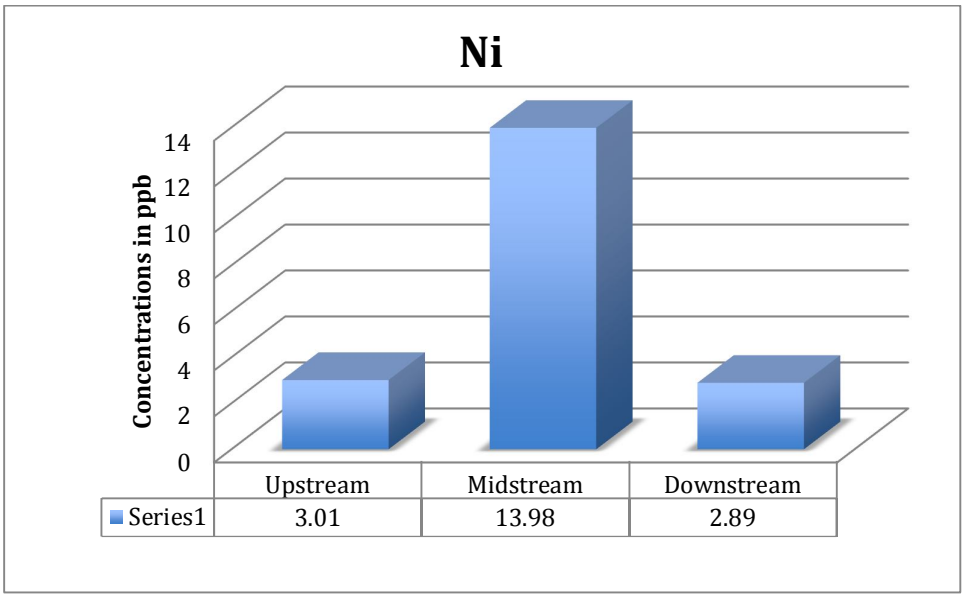


Figure 21. Nickel concentrations in surface water from upstream to the downstream of Kano River

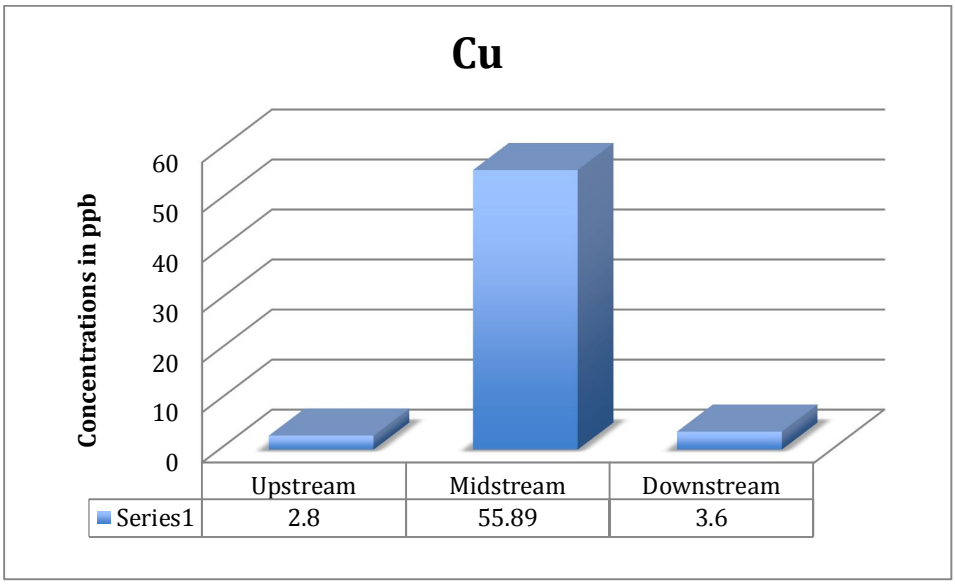


Figure 22. Copper concentrations in surface water from upstream to the downstream of Kano River

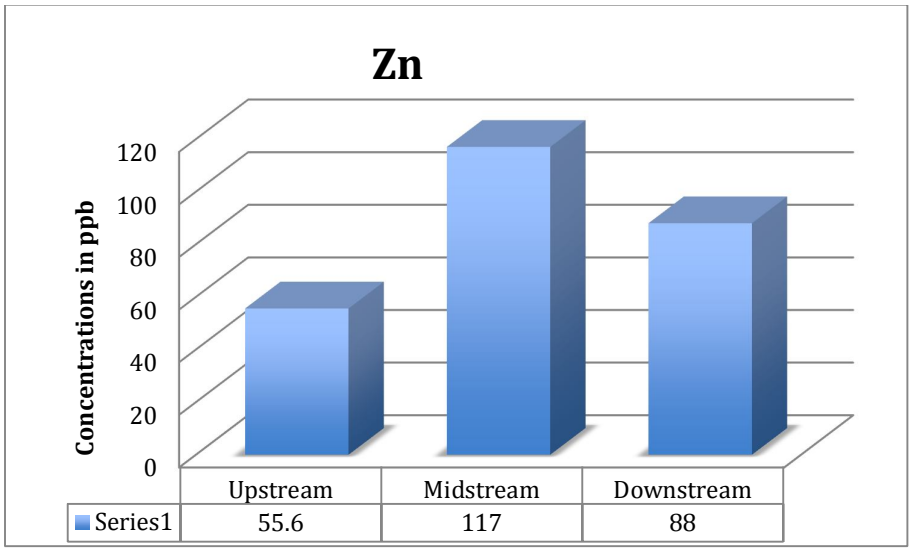


Figure 23. Zinc concentrations in surface water from upstream to the downstream of Kano River

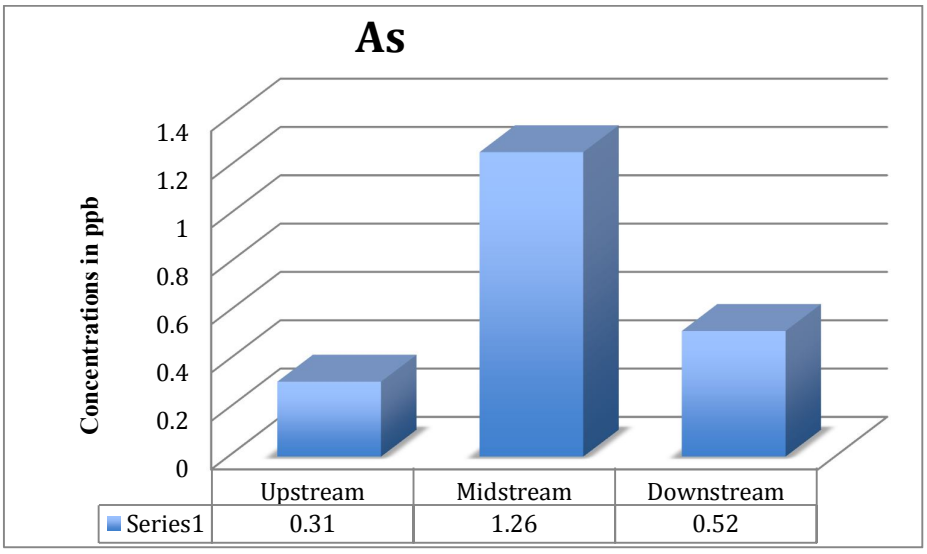


Figure 24. Arsenic concentrations level in surface water from upstream to the downstream of Kano River

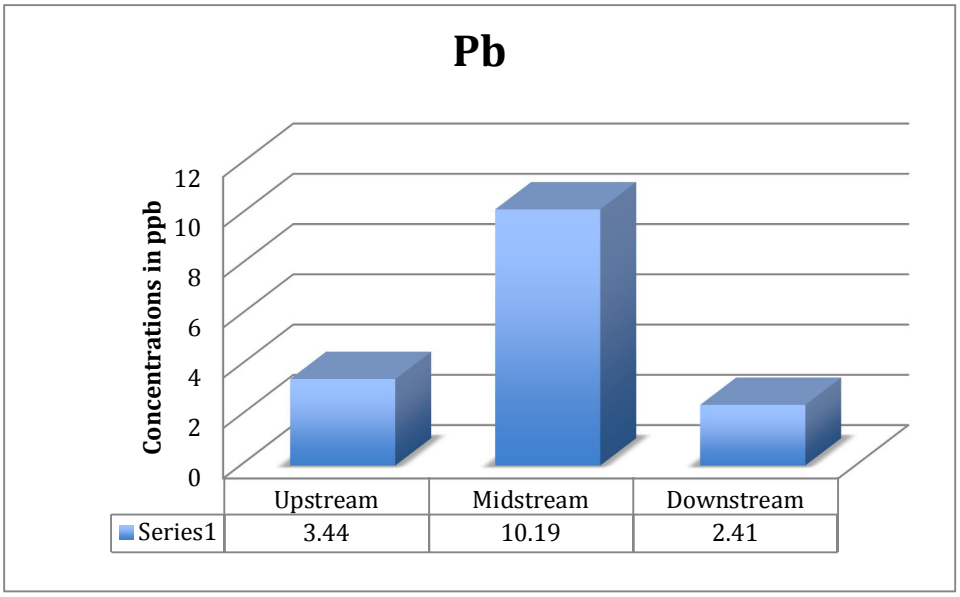


Figure 25. Lead Pb concentrations in surface water from upstream to the downstream of Kano River

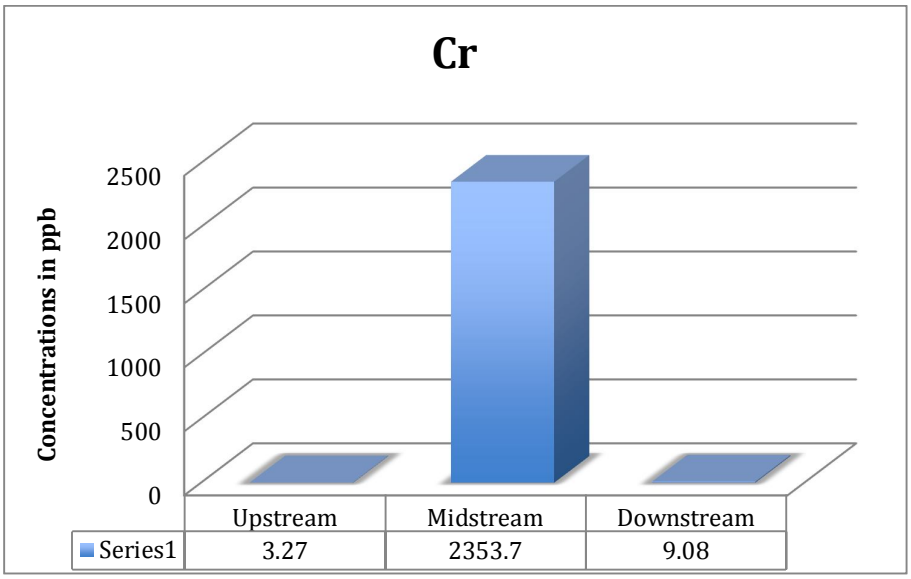


Figure 26. Chromium concentrations in surface water from upstream to the downstream of Kano River

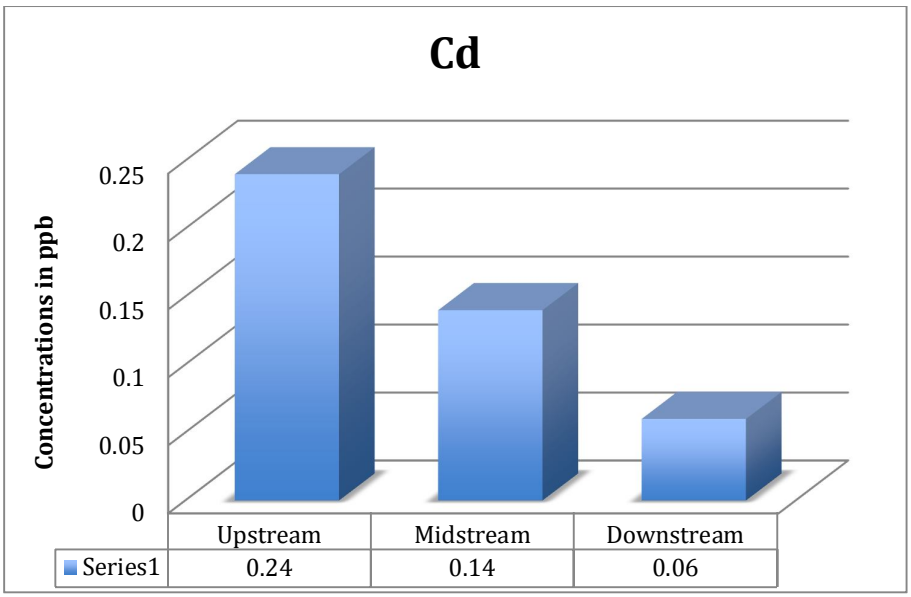


Figure 27. Cadmium concentrations in surface water from upstream to the downstream of Kano River

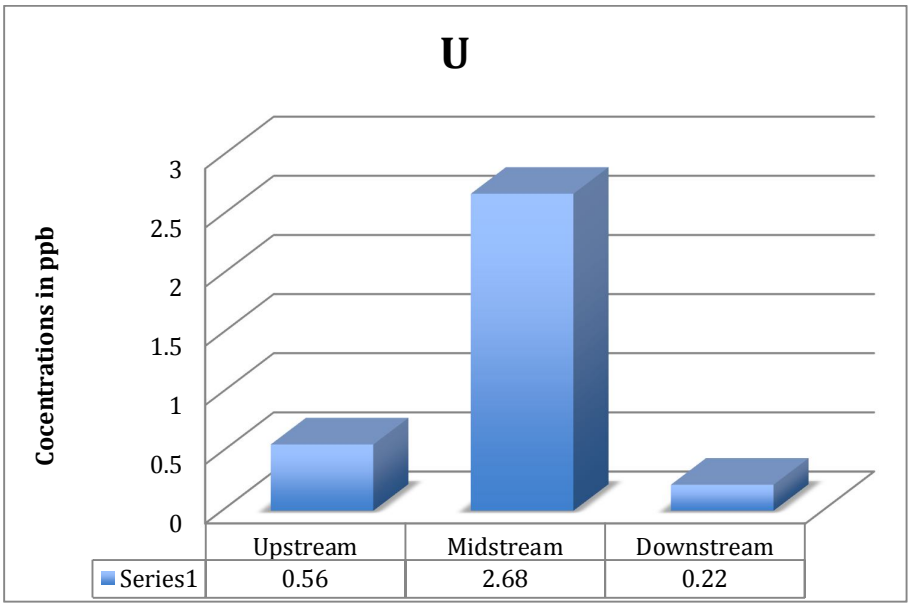


Figure 28. Uranium concentrations in surface water from upstream to the downstream of Kano River

Below, plate 11showing the impact of these heavy metals in surface water especially in fishing where important areas known as fishing points have now reduces the fish catch in these areas, which includes Wudil, Dabai, Gadar Ringim etc.



Plate 11. Gadar Ringim where fish catch is much done some year's back, but now this is what fishers get (07/03/12).

4.3 Comparison of Trends in both surface and groundwater

The concentrations of all the heavy metals analyzed in both surface and groundwater samples were compared, in order to observe the trend they manifest. The heavy metals includes V, Mn, Co, Ni, Cu, Zn, Cr, Cd and AS

Vanadium (V) in upstream groundwater shows a V shaped structure, suggesting the upstream concentration higher. This may be related to the geogenic factor and the dispersion is said to be natural through agents of weathering, erosion and dissolution. In the midstream V concentration is lower, where as in the downstream V concentration is higher and above standard levels. The reason may be tertiary as the water moves especially considering the river in the downstream is an an influent one; where the surface water recharges the groundwater.

In surface water, vanadium concentration is high in the midstream section. The trend in V concentrations shows a hill type structure, which means tertiary dispersion may be responsible especially industrial and household ones. Upstream vanadium concentration was low also as in the downstream.

Manganese (Mn) in concentration in the groundwater was high in the upstream and downstream. This is possible because the area through which the surface water flows rich in Zn, Cd Mn and Fe. Primary dispersion may probably be responsible for its high contents when compared with concentrations in the midstream side.

In surface water concentration of Mn is also high in samples from upstream. This is because the Mn flows into the surface water due to dissolution from primary and secondary dispersion (weathering, erosion and transportation/dissolution). Also tertiary dispersion is possible as the upstream side is a mining area.

Cobalt (Co) in groundwater has highest average concentration in downstream and midstream portions, lower than in the upstream. This may also results from tertiary dispersion and secondary dispersion when compared with surface water, Co concentrations is high in the upstream and downstream. It means the high concentration in groundwater may be due to infiltration in the process of recharging the groundwater by surface especially that the river turns into an influent drainage type.

Nickel (Ni) concentrations in groundwater is higher downstream but in the surface midstream concentration was higher. This means the concentrations in surface midstream may due to the tertiary disposition mainly from industrial and households sources that flows and recharges the downstream.

Copper (Cu) concentrations in groundwater from upstream and midstream groundwater are low and very high downstream. But in the surface water, Cu concentrations were high in the midstream and this may be related to tertiary disposition (industries and households). It is also worth noting to know that it is the midstream surface water that flows to the downstream and also recharges the groundwater because the area is sedimentary and it is also where the drainage turns into an influent one.

Zinc (Zn) concentrations in the groundwater from upstream and is higher than the downstream. Upstream concentrations in Zn may be related to primary disposition of Zn-Cd rich rocks (geogenic) of the area around Ririwai, where the river begins to flow from. The process of disposition may be weathering, erosion, transportation and then tertiary (mining) activity. In surface water highest concentrations is in the midstream and downstream. Primary disposition (weathering, erosion etc.) and tertiary disposition (Industries and households) are responsible for dissolving the Zn in water Upstream. Downstream Zn concentration may be

from the flow from midstream, especially that there may be no dilution from streams that empty into the Kano River, because the sample was taken in the dry season.

Arsenic (As) concentration is low in upstream surface water but high in midstream and down streamside. This also shows same trend with the groundwater midstream and downstream. There are the same high trends in the groundwater from midstream and down streamside. This means the flowing surface water is the same that goes and recharges the groundwater. It can be concluded based on the Arsenic content that the midstream surface is same as the groundwater, likewise the groundwater from both the midstream and downstream sides.

Lead (Pb) concentration in the surface water is highest in midstream, and is up to 10.19ppb. In the upstream the 3.44pp and this is related to the geogenic factors, as the area is rich in Zn-Cd, and Pb in its rocks, which is Younger Granite, ring complex. However, sources of Pb in the midstream are related to anthropogenic activities especially from industrial effluents. Downstream level of Pb concentrations is however low. Also Pb concentrations midstream was also high just as the surface water (same trend). Midstream in groundwater is 80.63pp then followed by the downstream of 12.91ppb. The reason for this is related to anthropogenic factors especially industrial effluents and the activities of smelting and recycling company in locality.

Chromium (Cr) concentrations in groundwater is high in the downstream side lowest in the surface water, it is highest is in midstream. This means that the midstream surface water is from the industrial discharge and when it flows downstream it affects species and also recharges the groundwater. Being in the downstream sides it changes into an influent drainage type.

Cadmium (Cd) concentration in surface water was higher in upstream and is related to geogenic factors, especially as the area is rich in Zn-Cd, Pb mineralization at Ririwai. The dispersion mode is weathering, erosion and also mining whereas it is low downstream. In groundwater highest concentration is in the downstream and may be related also to anthropogenic and geogenic factors.

4.4Comparison of levels of Heavy metals obtained in surface water with standards (EPA, 2004 and WHO (2011)

Locations of sampling points were labelled based on three categories (locations of samples) either from upstream, midstream or downstream of the river (figures 6 and 30). The concentration levels are also shown graphically and the standards were used as threshold. It is worth noting here to know that the standards used were configured into numbers as EPA, 2004 stands as 300 whereas, WHO, 2011 stands as 400 as used in the spider plot for easy understanding and interpretations.

Chromium (Cr) concentration results show that samples from metropolis (red colour) are high in almost all samples from that area are above the threshold of EPA (2004). In the upstream and downstream of the drainage basin (blue and green) their concentration values are below the threshold (Figure 30).Whereas based on comparison with WHO, 2011 all midstream concentration values are higher than the threshold. It is apparent that metropolitan Kano being an industrial area especially presence of tanneries which uses chromium in tanning and their waste being discharged into stream which then emptied into Kano river. This may be the reason for high concentrations values in surface water in the metropolis.

Nickel (Ni) concentration show that samples in red colour (Kano metropolis) is higher than the threshold (EPA, 2004), and those from upstream and downstream are below. Also this same when compared with WHO, 2011 threshold. Samples from midstream were all above this threshold too.

Manganese (Mn), this shows no clear distinction when compared with the EPA, 2004 threshold. It is also same with compared with WHO, 2011. This may be related probably to the geogenic factor for the fact that manganese are iron bearing rich especially in the crystalline complex and some contributions from the anthropogenic activities especially industrial ones.

Lead (Pb) concentration is high in the majority of the samples especially midstream (Kano metropolis) and are mostly above the threshold (EPA, 2004). On the other hand samples from midstream were also higher than the WHO, 2001 standard threshold.But it is noteworthy to remember that in the industrial area of Sharada a battery smelting company exist. Also samples of both ground water and surface at the company shows level of concentration of 865ppb in groundwater only. This can be observed from Figure 30 and 31 respectively.

Copper (Cu) concentrations in most samples were below the two thresholds in both locations except one from the midstream concentration values also exceed the threshold. Sources of copper concentrations are ascribed to the industrial effluents Figures 30 and 31.

Arsenic (As) concentration on the other hand all the samples concentrations values below the threshold. Concentration values from midstream were higher than other two (upstream and down stream). This is also ascribed to anthropogenic factor of industries especially dyeing and tanning industries.

Cadmium concentration values in all samples were below the two thresholds with only exception of one from upstream in Ririwai that ware all above the two threshold (Figure 30 and 31).

Uranium (U) values are all below the two threshold of (EPA, 2004 and WHO, 2011). High concentration values are in the midstream samples compared with those in upstream

and downstream. This may be tied to disposal of electrical appliances like televisions, bulbs etc. Were seeing inside river especially Kano river.

4.5 Comparison of levels of Heavy metals obtained in Groundwater with standards (EPA, 2004 and WHO, 2011)

Chromium concentrations levels from downstream are above the threshold of EPA, 2004. But all values when compared with WHO, 2101 threshold were below the threshold. It is important to note that those high concentration values were in the downstream and downstream samples were from the Chad Formations where surface water is an influent one. So high values in the ground water may be from the recharge it gets from the surface that is rich in chromium. Which is from industrial areas and domestic ones.

Nickel (Ni) samples are lower than the threshold with only exception of one sample from midstream. One thing to note here is those samples from midstream and downstream is high in concentrations than the upstream and this may be related to anthropogenic factor in the effect of high concentrations.

Lead (Pb) concentrations from midstream are high above the EPA, 2004 threshold, whereas, when compared with the other threshold of WHO, 2011concentrations were also above it. Samples from midstream and downstream especially. Reason attributed to this high levels in all samples may be from industries especially battery smelting ones and other related types. One sample from industrial area that was highest of all levels of concentrations can be seeing in Figure 32 and 33 respectively. Also one can see that in figure 33 and 34 one sample from upstream in Ririwai was also high and this may be related to geogenic factor especially that the area being from the Younger Granite area and this also shows same high lead concentrations in rocks of which the area is known in that.

Arsenic (As), concentrations in all samples are below the two thresholds. It can be observed that those from midstream are higher in concentrations than upstream and downstream. This may be from anthropogenic factor especially industrial type.

Cadmium (Cd), samples are below the two thresholds (EPA, 2004 and WHO, 2011). Those concentrations from upstream are higher than all others.

Copper (Cu), samples from midstream are higher and above the thresholds (Figure 32 and 33) than those in downstream and lowest are those from upstream. Here it can be said that the high levels may be from anthropogenic factor and also this levels shows the extent to which it has reached downstream in groundwater especially that downstream surface water is an influent one.

Manganese (Mn), most samples are below the thresholds and only few were above but with no clear distinction. Here manganese concentrations may be related to geology for the fact that as said earlier manganese is always in association with iron and iron is rich in the crystalline complex.

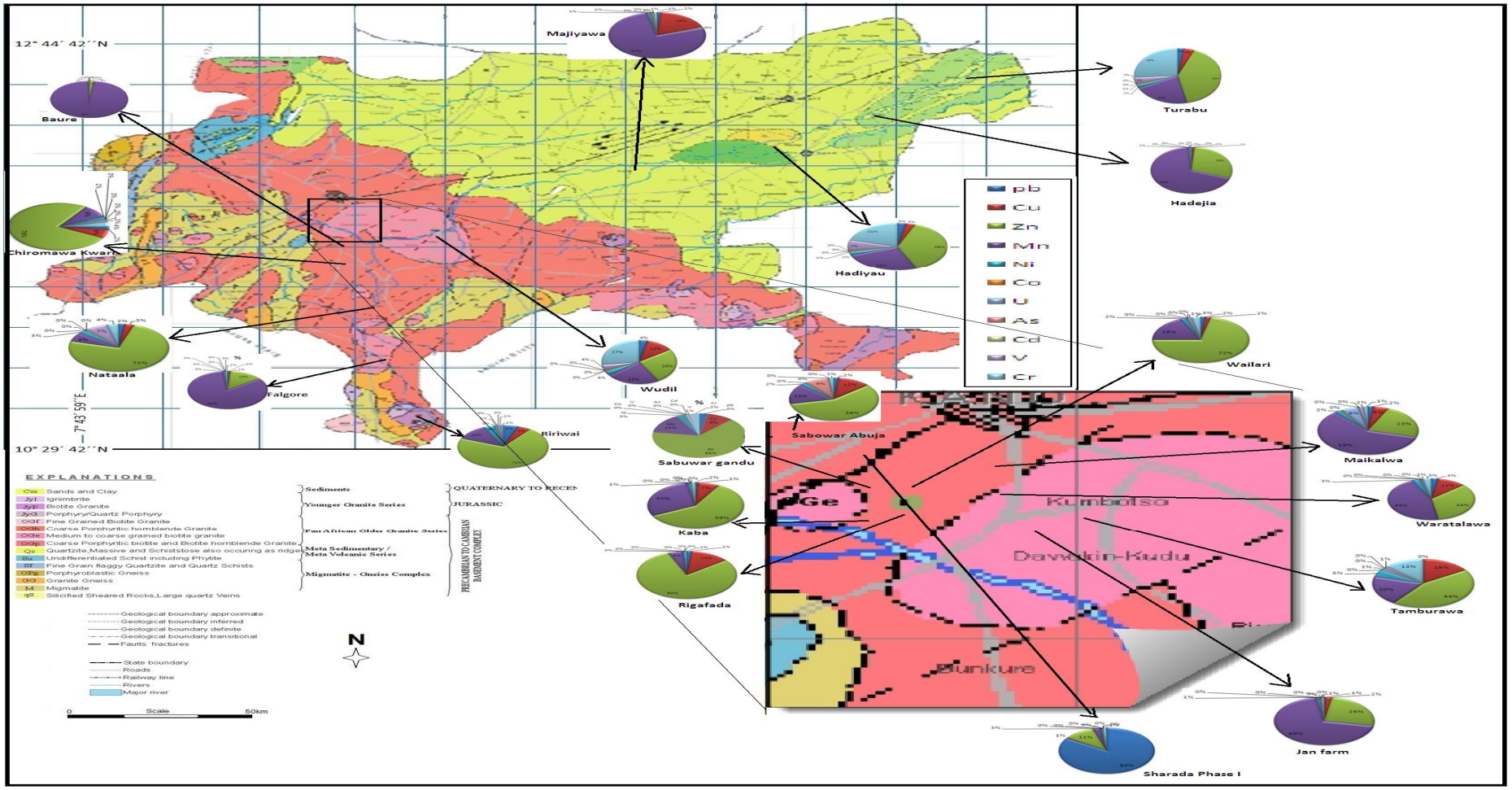


Figure 28. Map of concentration levels of heavy metals in surface water upstream, midstream and downstream of Kano river drainage basin.

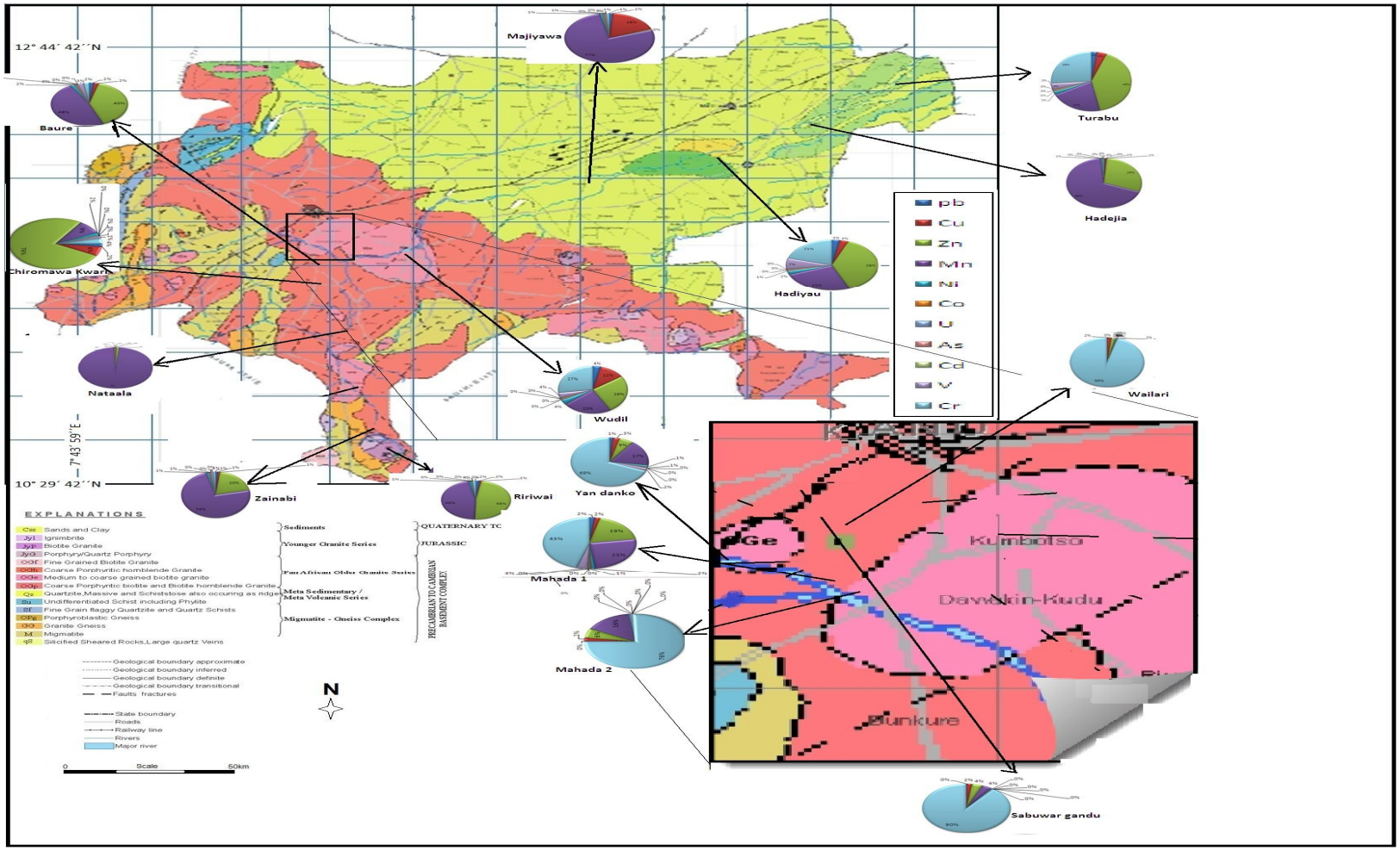


Figure 29. Map of concentration levels of heavy metals in groundwater in upstream, midstream and downstream of the Kano river to downstream of the drainage basin.

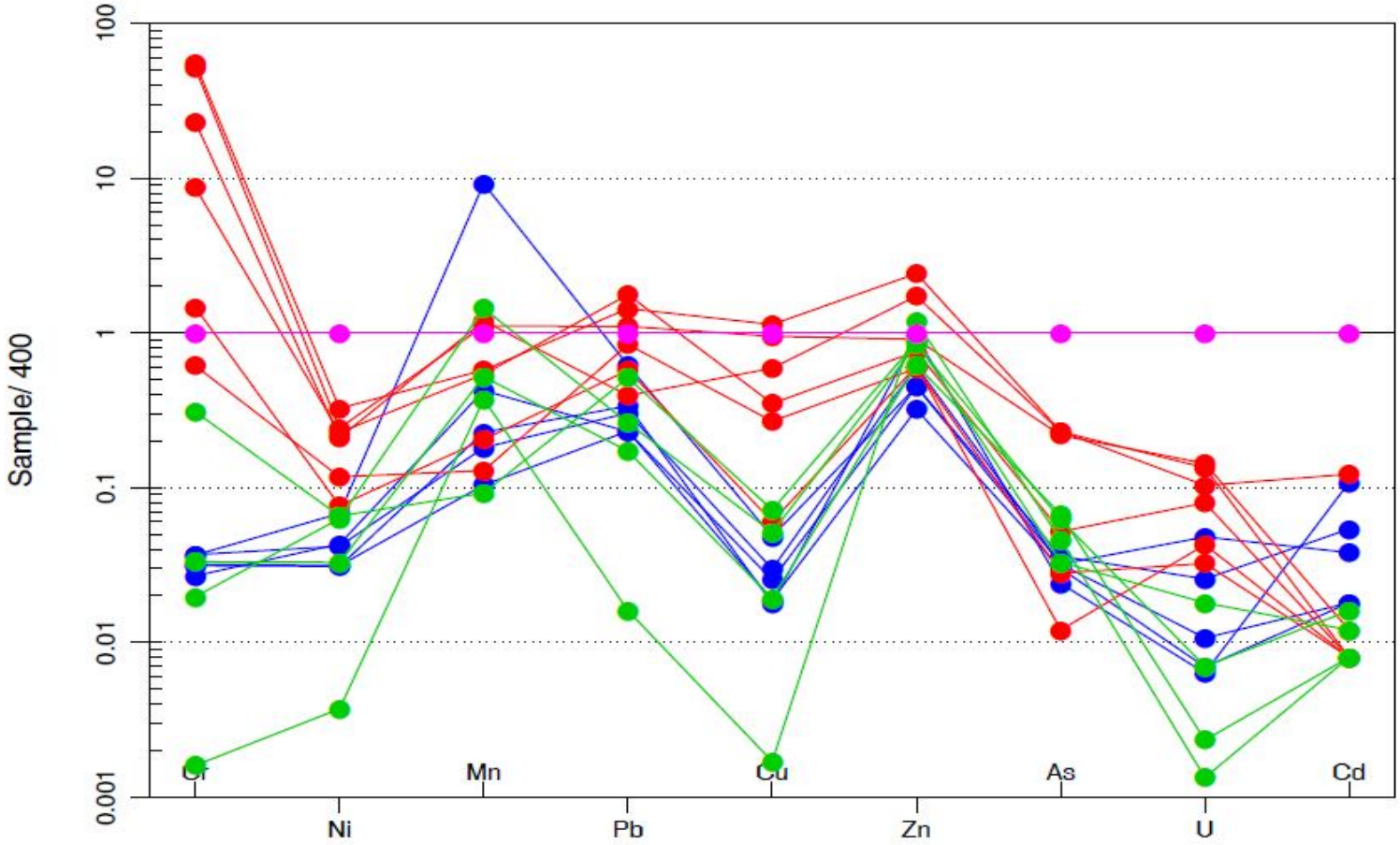


Figure 30. Concentration levels of heavy metals in surface water based on EPA 2004 Standards. Sample/400 means EPA 2004 in ppb
<u>EXPLANATIONS</u>: Red colours are samples from Midstream (Kano metropolis)
Blue colours are samples from Upstream (Ririwai – Karfi)
Green colours are samples from Downstream (Hadejia area)

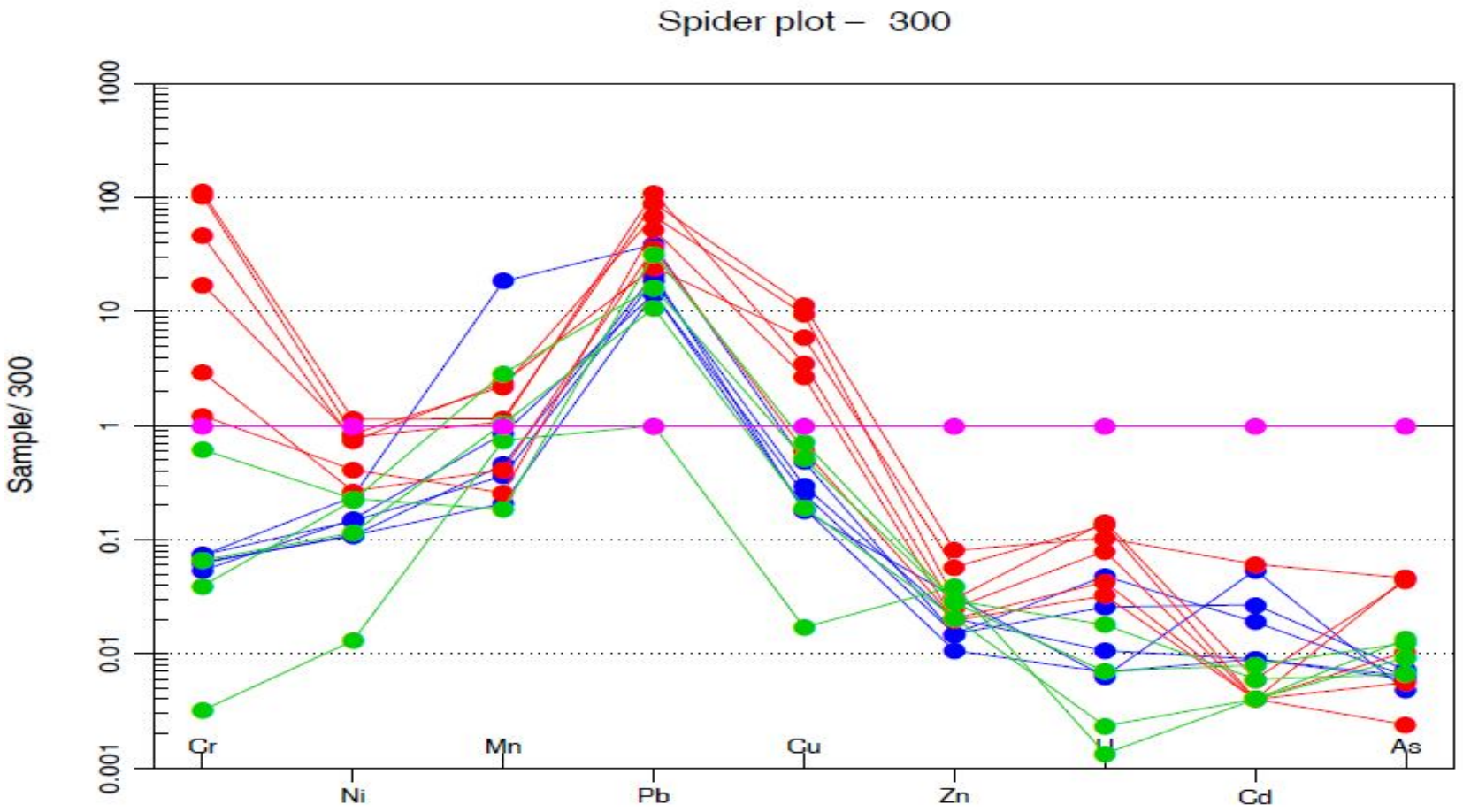


Figure 31. Concentration levels of heavy metals in surface water based on WHO 2011 Standards.Sample/400 means WHO 2011 in ppb

<u>EXPLANATIONS</u>: Red colours are samples from Midstream (Kano metropolis)

Blue colours are samples from Upstream (Ririwai – Karfi)

Green colours are samples from downstream (Hadejia area)

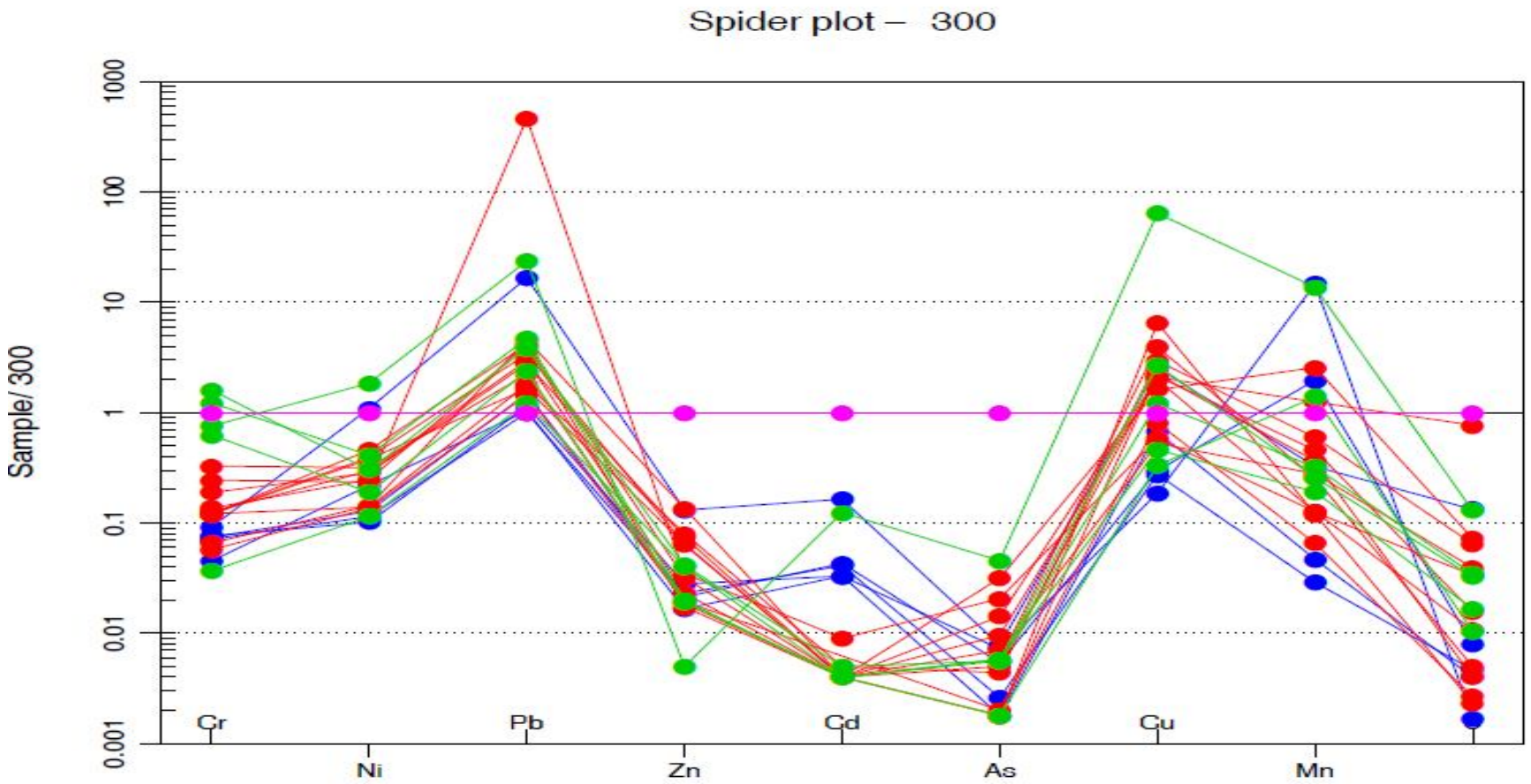


Figure 32. Concentration levels of heavy metals in groundwater based on EPA 2004 Standards. Sample/300 means EPA 2004 in ppb
EXPLANATIONS: Red colours are samples from Midstream (Kano metropolis)
Blue colours are samples from Upstream (Ririwai – Karfi)
Green colours are samples from downstream (Hadejia area)

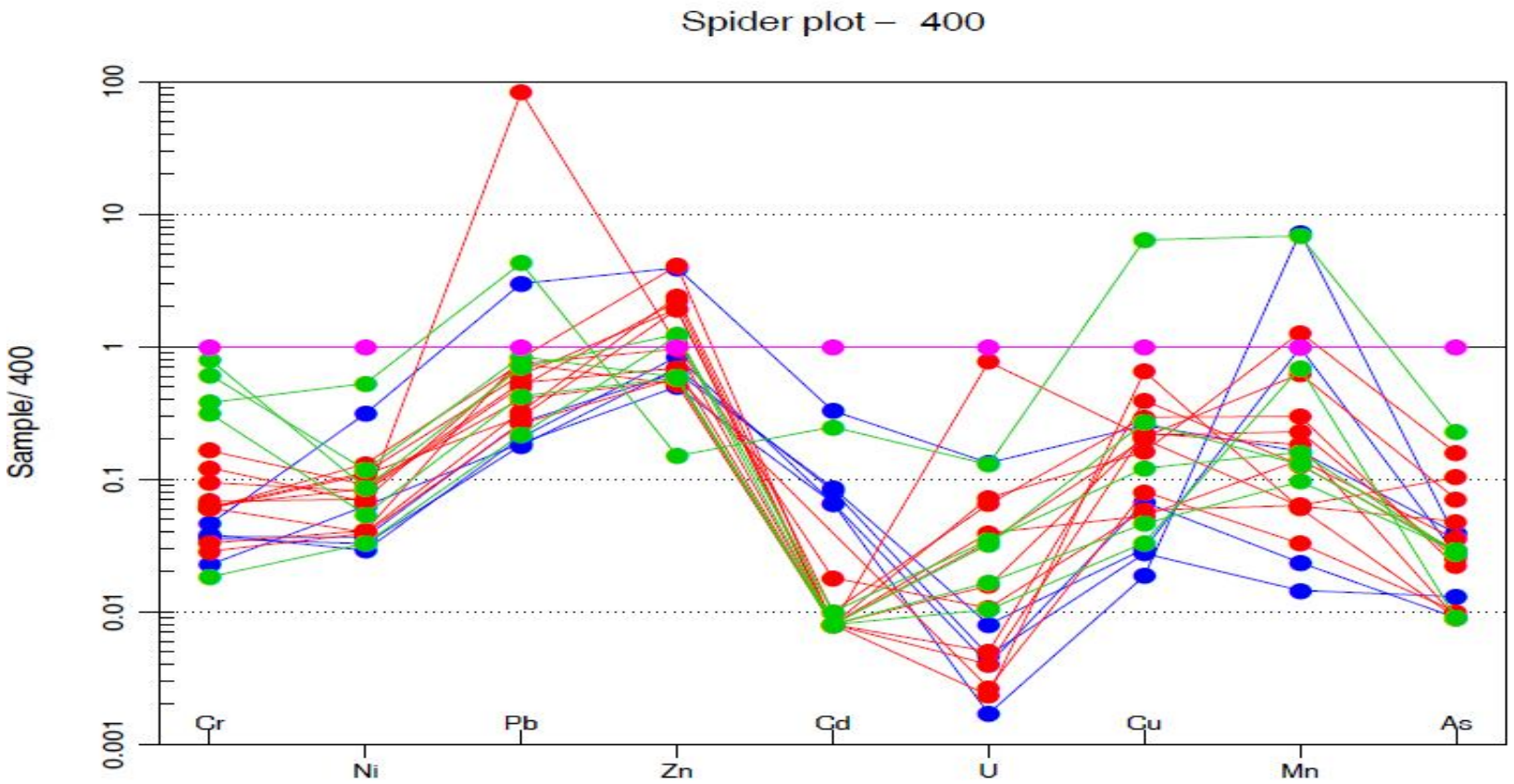


Figure 33. Concentration levels of heavy metals in groundwater based on WHO 2011 Standards. Sample/400 means WHO 2011 in ppb

<u>EXPLANATIONS</u>: Red colours are samples from Midstream (Kano metropolis)

Blue colours are samples from Upstream (Ririwai – Karfi)

Green colours are samples from downstream (Hadejia area

Table 4.11. Chemical Composition of Groundwater Upstream Kano River. Concentrations in parts per billion. Sampled by the Author, Analysed in the laboratory of the Institute of Foundation of Environmental Engineering of the Polish academy of Science in Zabrze.

No.	Lat.	Long.	V	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Cr	U	Remarks
173	$10^0$45.01	$8^0$43.49	5.54	64.88	0.81	21.86	25.49	393	0.39	1.64	30.04	4.59	3.98	Ni, Zn, Cd, U and Cu
176	$11^0$07.37	$8^0$34.34	1.22	392.92	0.47	2.56	2.98	64	0.27	0.43	2.68	3.68	0.24	
178	$11^0$15.45	$8^0$33.54	6.73	5.78	0.11	2.28	2.75	69	0.13	0.41	1.8	3.56	0.14	
179	$11^0$37.28	$8^0$21.58	1.54	9.37	0.11	2.03	6.7	84	0.09	0.33	2.07	3.83	0.12	
182	$11^0$50.46	$8^0$29.4	0.63	2922.2	5.21	4.39	1.86	50	0.36	0.33	1.87	2.26	0.051	Mn high may be lab mistake
Mean			3.132	679.03	1.342	6.624	7.956	132	0.248	0.628	7.692	3.584	0.906	
Maximum			6.73	2922.2	5.21	21.86	25.49	393	0.39	1.64	30.04	4.59	3.98	
Minimum			0.63	5.78	0.11	2.03	1.86	50	0.09	0.33	1.8	2.26	0.051	

NOTE: High Concentrations of elements listed in column remarks is probably related to industrial and domestic pollution

Table 4.12. Chemical Composition of Groundwater Midstream Kano Urban Area. Concentrations in parts per billion. Sampled by the Author, analysed in the laboratory of the Institute of Foundation of Environmental Engineering of the Polish Academy of Science in Zabrze.

No.	Lat.	Long.	V	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Cr	U	Remarks
195	**$11^0$52.09'**	**$8^0$30.07'**	**1.04**	**119.22**	**0.16**	**2.78**	**29.37**	**240**	**0.22**	**0.05**	**3.24**	**6.06**	**1.94**	
196	**$11^0$54.1'**	**$8^0$30.34'**	**0.44**	**24.11**	**0.24**	**2.86**	**64.95**	**408**	**0.09**	**0.04**	**8.25**	**3.29**	**0.07**	
197	**11055.06'**	**$8^0$32.22'**	**4.32**	**55.86**	**0.38**	**5.68**	**5.27**	**221**	**0.35**	**0.04**	**5.02**	**9.44**	**1.18**	
198	**$11^0$57.07'**	**$8^0$30.4'**	**1**	**13.05**	**0.18**	**2.72**	**8.05**	**58**	**0.1**		**2.62**	**2.86**	**0.08**	
199	**$11^0$57.48'**	**8030.32'**	**1.56**	**25.37**	**0.74**	**4.71**	**5.83**	**104**	**1.03**	**0.09**	**834.38**	**12.21**	**0.32**	**As, Pb, Cr, High**
200	**$11^0$55.43'**	**$8^0$32.43'**	**6.72**	**249.39**	**1.82**	**9.15**	**20.89**	**96**	**0.71**	**0.04**	**7.47**	**6.01**	**23.05**	**V, Co, Ni, As, and U are High**
202	**$11^0$53.59'**	**$8^0$27.24'**	**0.47**	**51.04**	**1.01**	**7.85**	**39.21**	**193**	**0.29**	**0.04**	**6.14**	**6.11**	**0.15**	
204	**$11^0$53.5'**	**$8^0$32.54'**	**1.17**	**91.34**	**0.48**	**5.92**	**21.45**	**69**	**0.25**	**0.04**	**5.34**	**6.31**	**0.47**	
205	**$11^0$52.14'**	**$8^0$31.54'**	**1.41**	**24.95**	**0.35**	**6.34**	**19.95**	**56**	**0.48**	**0.04**	**4.05**	**16.4**	**1.01**	**High in Cr**
206	**$11^0$52.54'**	**$8^0$31.22'**	**0.93**	**513.09**	**1.19**	**7.56**	**16.1**	**191**	**1.58**	**0.04**	**2.97**	**6.01**	**2.17**	**Mn, Co, As and U are High**
207	**$11^0$52.15'**	**$8^0$28.05'**	**0.59**	**72.84**	**0.17**	**4.94**	**22.28**	**52**	**0.09**	**0.04**	**7.41**	**6.81**	**0.12**	
Minimum			**1.7864**	**112.75**	**0.6109**	**5.501**	**23.03**	**153.5**	**0.472**	**0.046**	**80.626**	**7.41**	**2.778**	
Maximum			**6.72**	**513.09**	**1.82**	**9.15**	**64.95**	**408**	**1.58**	**0.09**	**834.38**	**16.4**	**23.05**	
Mean			**0.44**	**13.05**	**0.16**	**2.72**	**5.27**	**52**	**0.09**	**0.04**	**2.62**	**2.86**	**0.07**	

Table 4.13Chemical Composition of Groundwater downstream from Kano Urban Area. Concentrations level in parts per billion. Sampled by the Author, analysed in the laboratory of the Institute of Foundation of Environmental Engineering of the Polish academy of Science in Zabrze.

No.	Lat.	Long.	V	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Cr	U	Remarks
183	$12^0$07.35'	$9^0$10.08'	20.48	2742.4	21.24	37.01	640.9	15	2.27	1.24	42.69	37.82	3.87	V, Mn, Co, Ni, Cu, As, Pb, Cr are High
185	$12^0$21.4'	$9^0$55.17'	5.77	38.27	0.91	3.79	4.61	58	0.29	0.04	4.25	31.35	0.5	
188	$12^0$30.42'	$10^0$09.42'	10.56	63.93	1.82	6.03	12.08	124	0.28	0.05	6.98	80.18	1.04	
189	$12^0$26.31'	$10^0$01.59'	0.64	277.78	0.6	2.29	3.32	120	0.09	0.04	2.186	1.83	0.31	
191	$11^0$47.56'	$8^0$49.58'	8.56	51.56	1.41	8.21	26.83	59	0.28	0.04	8.42	61.38	0.97	
Mean			9.202	634.79	5.196	11.47	137.6	75.2	0.642	0.282	12.905	42.51	1.338	
Maximum			20.48	2742.4	21.24	37.01	640.9	124	2.27	1.24	42.69	80.18	3.87	
Minimum			0.64	38.27	0.6	2.29	3.32	15	0.09	0.04	2.186	1.83	0.31	

NOTE: High Concentrations of elements listed in column remarks is probably related to industrial and domestic pollution

Table 4.14 Chemical Composition of Surface water Upstream from Kano. Concentrations level in parts per billion. Sampled by the Author, analysed in the laboratory of the Institute of Foundation of Environmental Engineering of the Polish academy of Science in Zabrze.

No.	Lat.	Long.	V	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Cr	U	Remarks
174	$10^0$43.59′	$8^0$44.4′	0.39	91.16	0.14	2.17	1.79	95	0.24	0.54	3.37	3.13	0.19	
175	$10^0$47.43′	$8^0$46.5′	2.34	169.77	0.81	3.02	2.53	45	0.36	0.27	2.3	2.69	0.77	
177	$11^0$17.47′	$8^0$35.6′	7.51	3693.8	9.7	4.76	4.83	45	0.32	0.19	6.17	3.66	1.44	Co, Mn, Ni and U are High
180	$11^0$37.29′	$8^0$21.4′	2.44	41.58	0.56	2.19	1.88	32	0.3	0.09	2.32	3.18	0.208	
181	$11^0$50.51′	$8^0$29.4′	4.14	72.58	0.96	2.92	2.98	61	0.32	0.09	3.03	3.69	0.32	
Mean			3.364	813.778	2.434	3.012	2.802	55.6	0.308	0.236	3.438	3.27	0.5856	
Maximum			7.51	3693.8	9.7	4.76	4.83	95	0.36	0.54	6.17	3.69	1.44	
Minimum			0.39	41.58	0.14	2.17	1.79	32	0.24	0.09	2.3	2.69	0.19	

NOTE: High Concentrations of elements listed in column remarks is probably related to industrial and domestic pollution

Table 4.15 Chemical Composition in Surface water midstream from Kano Urban Area, Concentrations in parts per billion. Sampled by the Author, analysed in the laboratory of the Institute of Foundation of Environmental Engineering of the Polish Academy of Science in Zabrze.

No.	Lat.	Long.	V	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Cr	U	Remarks
192	$11^0$47.56′	$8^0$49.6′	8.56	51.56	1.41	8.21	26.83	59	0.28	0.04	8.42	61.38	0.97	Cr, Ni and Cu
193	$11^0$50.51′	$8^0$30.3′	12.28	81.86	2.11	5.35	6.02	61	0.12	0.04	5.75	146.76	1.28	Cr, and U are High
194	$11^0$50.43′	$8^0$30.34′	9.08	477.48	4.64	14.69	59.07	173	2.3	0.04	3.93	2317.1	4.03	Cr, U, Ni, Cu and U are High
201	$11^0$55.25′	$8^0$32.1′	7.89	443.9	4.57	16.93	95.06	91	2.18	0.06	11.01	5169.6	4.3	As, Pb, Cr, Ni, Cu and U are High
203	$11^0$52.46′	$8^0$28.2′	22.7	216.04	5.09	15.92	34.97	76	0.52	0.04	17.69	870.14	2.39	Pb, Cr, Ni, Cu and U are High
208	$11^0$57.28′	$8^0$30.5′	10.81	230.03	5.39	22.76	113.38	242	2.31	0.61	14.36	5557.4	3.1	As, Pb, Cr, Cu, and U are High
Mean			11.887	250.145	3.8683	13.977	55.888	117	1.285	0.1383	10.193	2353.7	2.67833	
Maximum			22.7	477.48	5.39	22.76	113.38	242	2.31	0.61	17.69	5557.4	4.3	
Minimum			7.89	51.56	1.41	5.35	6.02	59	0.12	0.04	3.93	61.38	0.97	

NOTE: High Concentrations of elements listed in column remarks is probably related to industrial and domestic pollution

Table 4.16. Chemical Composition in Surface water Downstream from Kano Urban Area. Concentrations in parts per billion. Sampled by the Author, analysed in the laboratory of the Institute of Foundation of Environmental Engineering of the Polish academy of Science in Zabrze.

No.	Lat	Long	V	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Cr	U	Remarks
184	**$12^0$08.03'**	**$9^0$09.5'**	**0.09**	**149.03**	**0.25**	**0.26**	**0.17**	**118**	**0.46**	**0.04**	**0.16**	**0.16**	**0.04**	
186	**$12^0$21.55'**	**$9^0$55.1'**	**6.03**	**36.91**	**0.99**	**4.59**	**7.17**	**88**	**0.33**	**0.06**	**5.13**	**30.88**	**0.54**	**Cr high**
187	**$12^0$30.4'**	**$10^0$09'**	**0.13**	**575.43**	**1.93**	**4.41**	**5.14**	**84**	**0.62**	**0.08**	**2.62**	**1.97**	**0.21**	
190	**$11^0$47.56'**	**$8^0$50'**	**0.09**	**208.27**	**1.74**	**2.3**	**1.92**	**62**	**0.67**	**0.04**	**1.72**	**3.31**	**0.07**	
Mean			**1.585**	**242.41**	**1.2275**	**2.89**	**3.6**	**88**	**0.52**	**0.055**	**2.4075**	**9.08**	**0.215**	
Maximum			**6.03**	**575.43**	**1.93**	**4.59**	**7.17**	**118**	**0.67**	**0.08**	**5.13**	**30.88**	**0.54**	
Minimum			**0.09**	**36.91**	**0.25**	**0.26**	**0.17**	**62**	**0.33**	**0.04**	**0.16**	**0.16**	**0.04**	

NOTE:High Concentrations of elements listed in column remarks is probably related to industrial and domestic pollution. Also Chromium in column remarks represent probably the extent of chromium pollution fro Kano urban areas.

Laboratory Work group:Prof. RajmundMichalski, MS Joanna Kernert, MS HalinaMęrek, MS Sebastian Szopa, MS IzabelaFidyka, KatarzynaStah

Table 4.17. Summary and Comparison of levels of Concentrations of Heavy Metals in Water with WHO (2011), EPA (2004) and NIS (2007) Guidelines.

Parameter	Unit	EPA (2004) ppb	NIS (2007) ppb	WHO (2011) ppb	The Study Area (ppb) Range	Mean	Remarks
V	ug/L				0.09 - 22.78	4.81	
Mn	ug/L	400	50	200	5.78 - 3693.8	405.98	Above limit
Co	ug/L				0.11 - 21.24	2.26	
Ni	ug/L	70	-	20	0.26 - 37.01	7.37	Within limit
Cu	ug/L	100		10	0.17 - 640.93	37.62	Above WHO limit
Zn	ug/L	100	5000	3000	15 - 408	115.03	Above limit by EPA
As	ug/L	10		50	0.09 - 2.31	0.62	Low
Cd	ug/L	5		10	0.04 - 1.64	0.21	Slightly low
Pb	ug/L	0	15	10	0.16 - 834.38	29.82	Above limit Off all the guidelines
Cr	ug/L	100	100	50	0.16 - 5557.35	419.58	Above all standards guidelines
U	ug/L	30	30	-	0.04 - 23.05	1.75	Within limit

Laboratory Work group: ***Prof. RajmundMichalski, MS Joanna Kernert, MS HalinaMęrek, MS Sebastian Szopa, MS IzabelaFidyka, KatarzynaStah***

4.5.2 Major ions in both water samples

Na ranges from 3.65 – 970 ppm and average of 105.156 ppm, K ranges from 2.72 - 43.57 ppmand average of 19.385 ppm, Ca ranges from 3.22 - 66.79 ppm and averaged of49.655 ppm, Mg ranges from 0.06 -3 2.07 ppb and an average of 10.616 ppm, all in milligrams per litre or parts per million. Also for the anions in the water of the area HCO_3 ranges from 27.46 - 486.24 ppm and average **of** 277.902 ppm, NO_3 ranges from 0.94 - 226.65 ppm and average of 15.631 ppm, Franges from 0.06-8.58 ppm and an average of 4.326 ppm and Br and $PO_4$of ranges 1.2 - 69.22 ppm with average of 4.326 - 1.26 ppm and average of 1.26 ppm. Cl ranges from 0.08 – 116.25 ppm with an average of 15.25 ppm.Table 4.18 below shows the results of concentrations level obtained compared with WHO, 2011, EPA, 2004 and NIS standards.

Table4.18 Summary of Results with Comparison of Studied Parameters in the Studied Water Samples on Major ions with WHO (2011), EPA (2004) and NIS (2007) Note that TDS measured in the field proves highly inaccurate and therefore disregarded. TDS obtained from additions of ions are accepted. Guidelines.***Naturally occurring chemicals whose guidelines were not established by WHO so their values are proposed or secondary guidelines.** ***Laboratory Work group: Prof. RajmundMichalski, MS Joanna Kernert, MS HalinaMęrek, MS Sebastian Szopa, MS Izabela Fidyka, Katarzyna Sta***

Parameter	Unit	EPA (2004)	NIS (2007)	WHO (2011)	The Studied Area work (Range)	Mean from the worked area	Remark
Temperature	oC	-	-				Not regulated
Conductivity	US/cm	-	1000	1400			
Total Hardness	Mg/L	-	150	500			
*TDS	Mg/L	500	500	1000	7 - 128	24.79	Within limit
*pH	pH	6.5-8.5	6.5-8.5	6.5-8.5	6.6 - 8.5	7.18	Slightly higher
Ca	Mg/L			75	3.22 - 128.81	25.56	Within limit
Mg	Mg/L		0.2	50	0.06 - 175.17	10.62	Higher than limit
*Na	Mg/L	-	200	50	3.65 - 970.48	54.17	Within limit by NIS
*K	Mg/L	-	-	55	2.72 - 52.52	9.98	Within limit by NIS
HCO_3^-	Mg/L	-	-	1000	2746 - 4863.3	277.9	Within limit
*SO_4^{2-}	mg/L	250	100	250	2.15 - 147.1	11.27	Within limit
*Cl	Mg/L	250	250	250	0.08 - 116.19	15.25	Within limit
NO_3	mg/L	10	50	50	0.94 - 47.49	8.09	Within limit
PO_4	mg/L				1.26 - 1.26	1.26	No guideline
Cl	mg/L	250	250	250	0.08 – 116.25	15.25	Within limit
F	Mg/L			1.5	0.06 - 8.58	4.40	Very Higher

4.6Water Classification

4.6.1 Classification of Water Types based on major ions contents

(a) Piper Diagram

Piper diagram was produced and this is based on concentrations of ions detrmined from the water sample. Here a plot of maro elements (cations) of the analyses were done on triangle togather with their respected anions and this was projected in a diamond shaperepresenting both cations and the anions and their relationships was detrmined. From their plots, water types is determined.

(b) Schoeller Diagram

This diagram uses vertical scale diagram. Here ion concentrations are plotted in mg/l in sequence with Ca^{++}, Mg^{++}, Na^{+}, Cl^{-}, $S0_4$, and also HCO_3 on vertical axix with use of a logarithmic sacle . Point that have same chemical analysis are then connected with a straight lines therefore revealing differnt classes of water. Here actual ionic concentrations are displayed and potrayed. Most interesting part of this diagram is it can accomodates many combinations of ions. This diagram was developed in order to indicates Cl^{-} ,$S0_4^{2-}$, and HCO_3 in the sample taken and results shows that there is variations between Cl^{-} and HCO_3 and SO_4^{-} , but not much between HCO_3 and SO_4. There is a considerable variattion between Mg+ with Na and Ca^{++} i.e Mg^{+} vary most.

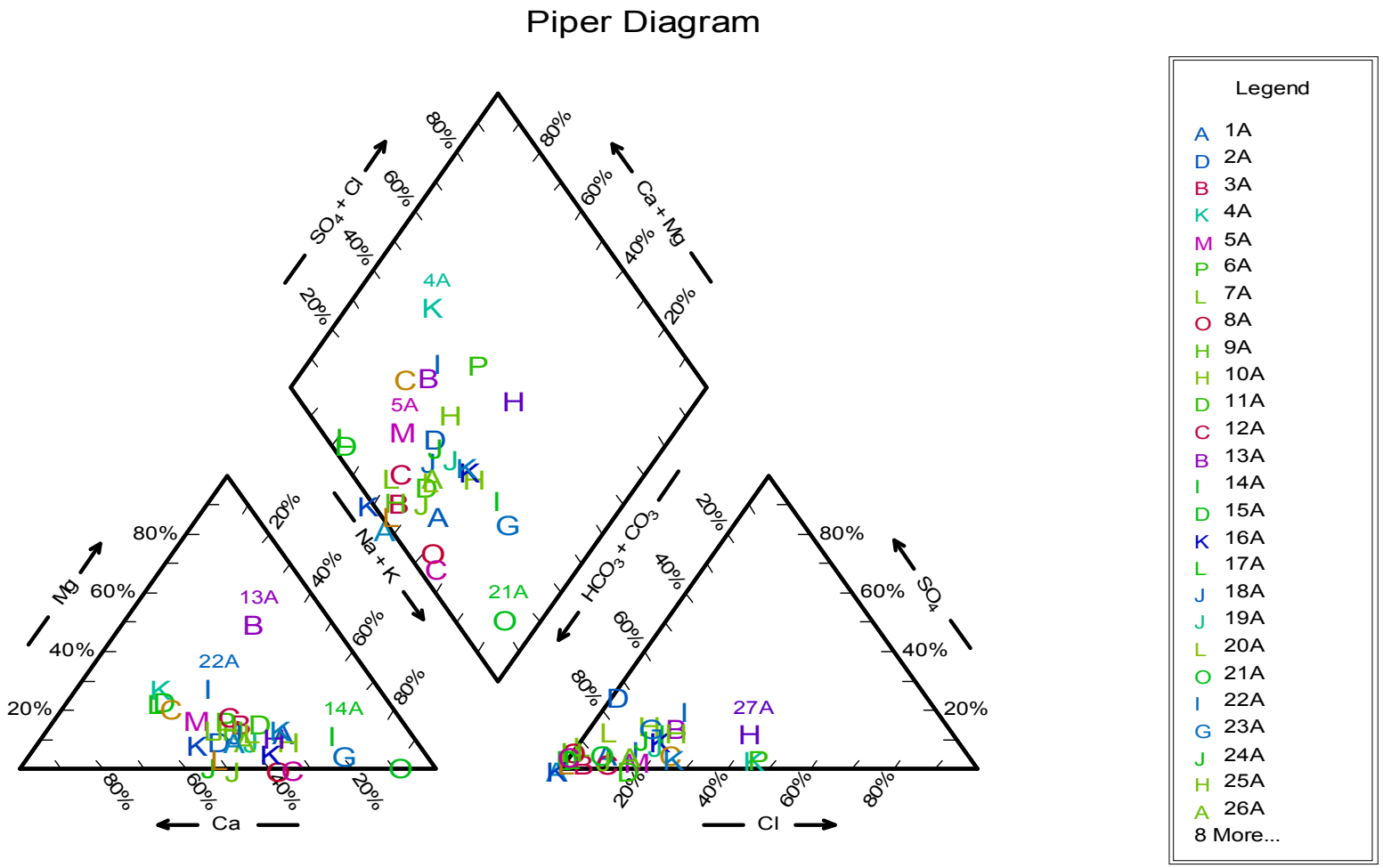


Figure 34. Plot of ions in the studied area (both groundwater and surface water samples) on Piper Diagra

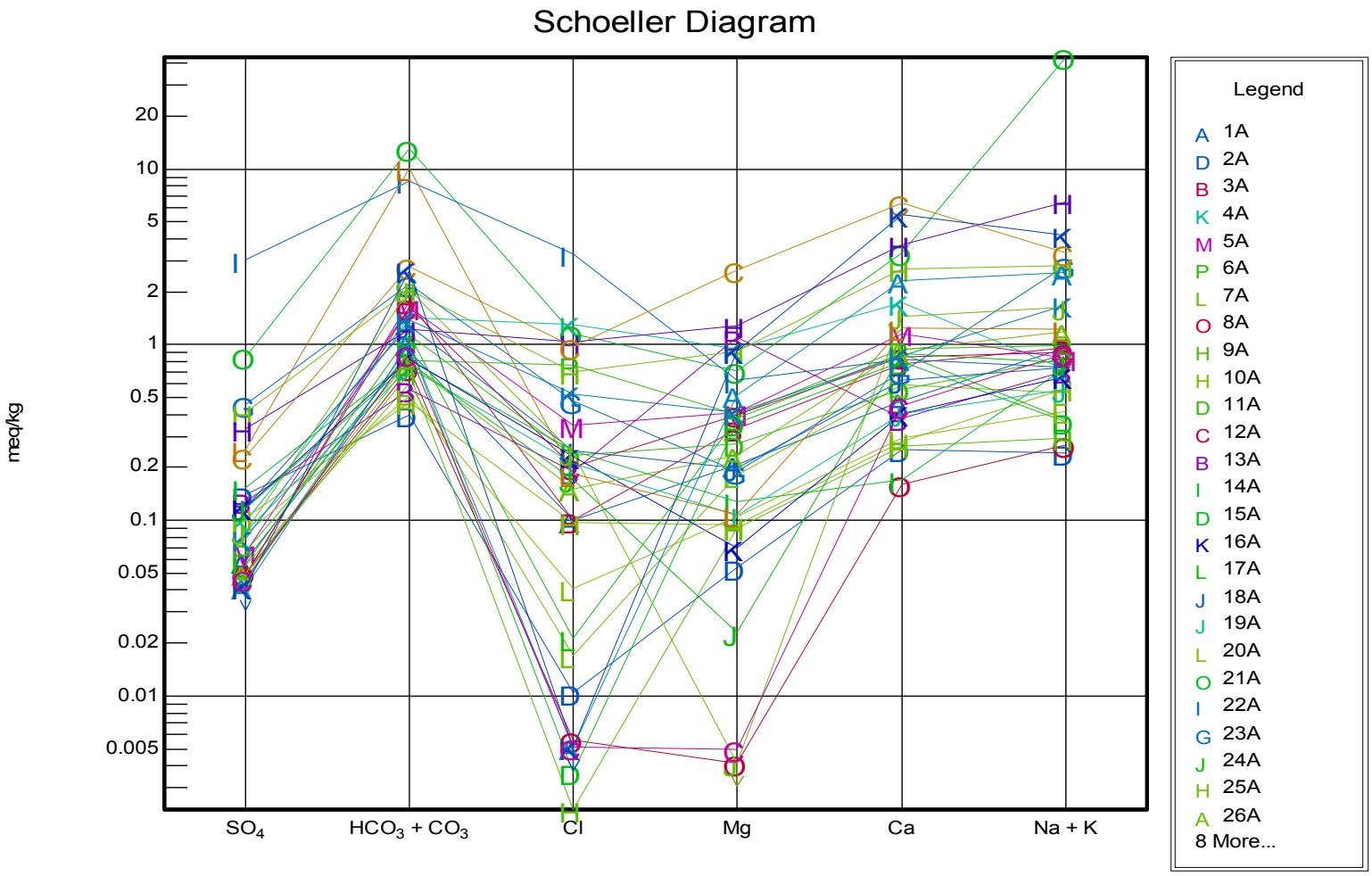


Figure 35. Plot of Schoeller Diagram in the studied area both (groundwater and surface water) of the major ions and minor elements.

4.6.2 Water Types of the Studied Area

This is based on the concepts of numerical evaluation of the chemical analyses all based on the relationships' between the ions in water that forms the water types. Water type in the study area indicates that based on 35 samples the majority base on the crystalline and Chad Formation water types are **$NaHCO_3$** types with 18 sample indicating that based on **AQQA Rock ware** software and also 16 samples are **$CaHCO_3$** and only one (1) indicated as **$MgHCO_3$** type. Also based on Sodium hazards according to Richard (1954) the remarks in table 4.19 shows levels obtained of which 21 samples are S1 types which means they are in bracket of excellent. Also none of the samples was doubtful and eleven were found to be un suitable. Table 4.19 below shows the sodium hazard.

Table 4.19. Sodium Hazard in the study area Based on USSL Classification by (Richards, 1954); S1- Excellent, S2- Good, S3- Doubtful and S4and 5- Unsuitable

Sodium Hazard	SAR equivalent per mole	Number of Samples from the Study area	Remark on quality
S1	10	21	Excellent
S2	10-18	-	Good
S3	18-26	-	Doubtful
S4&S5	>26	11	Unsuitable

Also based on salinity hazards according to Richards (1954) it was determined that 25 of all the samples are excellent and 8 were good and only 2 are doubtful. Table 4.20 below shows the classification according to Richard (1954). This classification is based on electrical conductivity compared with one obtained from the study area.

Table 4.20 Salinity Hazards in the study area according to Hazard is low Richard, 1954 classification. C1-Excellent, C2-Good, C3- doubtful and C4 - Unsuitable

Salinity hazard	EC (microhms/cm)	Result from the study area	Remark on quality
C1	100-250	25	Excellent
C2	250-750	8	Good
C3	750-2250	2	Doubtful
C3&C4	>2250	-	Unsuitable

4.7 Suitability of Water for Various Uses

4.7.1 Suitability of water for Drinking and Domestic use Based on Major Ions and Heavy Metals Determined in the Study Area

The suitability of water for drinking and domestic use varies from one country to another; therefore, some standards and guidelines were compared with to ascertain the water of the area for various kinds of uses. These standards and guides includes WHO (2011), EPA (2004) and NIS (2007). Based on data analysed water of the area was categorised and classed for drinking and domestic use.

pH in the area ranges from 6.25 to 8.7with a mean concentration level of 7.17 and based on NIS (2007) is 6.5 to 8.5, EPA (2004) 6.5 to 8.5 and WHO (2011) 6.5 to 8.5. From this it means that the water is slightly alkaline but within tolerable ranges of all the three guidelines so that water can be said to be within range for drinking and domestic use.

TDS ranges from 7 to 128 with mean concentration level of 24.79 mg/l and based on the three guidelines of NIS (2007), WHO (2011) and EPA (2004) is 500 each and from the average obtained in the study area water can be said to be within limit and useful in drinking and domestic (Even though the result measured in the field is disregarded).Na in the study area ranges from 3.65 to 970 ppm and a mean concentration level of 105.156 ppm and based

on the three standards and guidelines used for comparison is 250 ppmso water in the study area is far below the standard and water is good for both domestic and drinking purposes**.**

K in the study area ranges from 2.72 to 43.57 ppmand mean concentration level of 19.38 ppm and in comparison with the three standards only WHO (2001) sets 1000,and the study area has mean of 19.39 ppm so water is far below the standard and excellent for drinking and domestic uses is good to note that Na content in water is not important except sick people and when in high concentrations with sulphate leads to laxative gastro internal irritation.

Low Nais only desired for patients with heart, kidney ailments and pregnant women.

Ca in the study area ranges from 3.22 to 66.79 ppm and mean concentration level of 49.655 ppm and in comparison with the three standards only WHO (2011) sets 75 ppm. Therefore water is good for domestic and drinking use and is far below the level of the standard. Even though Ca is troublesome and is known for its role in humans in scale formation. Mgin the study area ranges from 0.06 to 32.07 ppb and mean concentration level of 10.616 ppm.

Cl in the study area ranges from 0.08 to 116.25 ppm with a mean concentration level of 15.25ppmand based on the three compared standards water is far below the limit and therefore good for drinking and domestic use.

HCO_3in the study area ranges from 27.46 to 486.24 ppmwith mean concentration level of 277.902 ppmfar less than WHO (2011) standard of 1000 ppm and the rest were silent**.** NO_3 in the study area ranges from 0.94 -226.65 ppmwith mean concentration level of 15.631 ppmwithin limits of all the three standards. Fin the study area ranges from 0.06 to

8.58 ppmwith means concentration of 4.326 ppm. PO_4in the study area ranges from4.326 to 1.26 ppm and means concentration level of 1.26 ppm.

4.7.2 Suitability of Water for Irrigation Based on Major Ions and Heavy Metals Determined in the Study Area

In irrigation water there are many things that are considered and include Bicarbonate hazard, Na hazard, salinity hazard, toxic elements hazards, suspended solids hazards and then pathogenic hazard which is mostly biological in nature.

Salinity is based on the levels of 250, 750, 2250μs/cm of conductivity, but water from the study area shows that all are not up to 250μs/cm,so it then means that the water is generally good for irrigation based on salinity contents (both surface and groundwater).

Another of interest is the one considered special for this research if toxic element mostly called heavy metals and these includes boron, cadmium, lead, chromium, selenium, arsenic and fluoride. Cadmium in irrigation water should be present at concentrations below 10 ppb; in the study area has ranges from 0.04 to 1.64 ppb with an average of 0.206 ppb.

4.7.3 Suitability of Water for Livestock watering Based on Major Ions and Heavy Metals Determined in the Study Area

It is known that animals can tolerate water of much poorer quality than that of domestic use by human, limits accepted in clause from drinking and domestic use could be exceeded. Most important values are TDS, and also even TDS **is** 5,000 ppmi.e. permissible. On the other hand the study area none of the results exceeds this permissible limit ranges from 7 to 128 with mean concentration level of 24.79 ppb**,** so water based on TDS can be said to be good for livestock watering but the reservation is based on TDS contents only.

In livestock watering another consideration is also made based on toxic elements or heavy metals contents, even though animals are more tolerant due to their short life span. But, their accumulated toxicity can be transferred to their end users (humans). Maximum

permissible limit for Cadmium is 50 ppb, in the study area 0.04 to 1.64 ppb with an average of 0.206 ppb so water is good for livestock watering based on cadmium contents.

Maximum of Pb is 100 ppb and water in the study area ranges from 0.4 to 192.69 ppb and an average of 22.17 ppb, of course there are some exceptions on this and this is found in the metropolis near a lead smelting company and in the area both surface and groundwater are above limits therefore is generally not good for livestock and objectionable for this use.

Crin the study area varies from 0.16 to 5557.35 ppb with an average of 419.58 ppb even though it limits is 1000 ppb but is likely going higher so if care is not taken there may be a risk in using the water for watering livestock. This can occur when all when factors responsible for its contents increase, it may then reaches limits and or go beyond.

This is also same with Pbwithin the objectionable limits or guideline especially those results obtained from the mid stream which coincidentally is the Kano Metropolis' especially surface water from the Kano River (Table 10). Asfor animals is 200 ppb in the study area ranges from 0.09 to 2.3and average of 0.62 ppb this is less than the guideline so water is good based on as contents in water of the study area.

In conclusion of the above suitability of water for livestock watering there is reservation especially water from the midstream or Kano metropolis and more importantly surface which from the Kano river is generally high in contents of heavy metals like Pb, CdandCr**.**

4.7.4 Suitability of Water for Engineering Constructions Based on Major Ions and Heavy Metals Determined in the Study Area

Water to be use for construction and concrete with cement and aggregates must be physically and chemically clear with turbidity of less than 5 Nephelometric Units (NU). In the study area highly turbid water is seen especially in the midstream up to Wudil this may be related

to the impact of sand mining which is taking place in the metropolis especially with the constructions of many project by the government on housing and other development constructions in the state. Unfortunately if water of these rivers is used in concrete making it reduces strength of the concrete. This may be a contributing factor in most ofthe cracks of in most new buildings in Wudil and some parts of the state.

4.8Heavy Metal Concentrations in Lithological Units.

4.8.1 Preamble

Natural quality of water is a function of the geochemical character of the rocks underlying the study area, and as such the concentration levels of heavy metals in the representative rock samples were determined and the results are shown in Tables 4.19 and 4.20. Average values of the heavy metals concentrations on the results obtained and compared with the crustal average similar to Taylor, (1964) as adopted by Brian mason (1966) averages for granites and basalts in the proportion 1: 1. Most minerals in rocks are soluble in water under appropriate geochemical conditions (Clayton, 1979).

Heavy elements are toxic due to their cumulative behaviour (Ndokwara and Ezihe, 1990). The lithological units in the area identified from upstream to downstream are as follows:

Volcanic rock (Ignimbrite); coarse porphyritic biotite hornblende granite; medium to coarse-grained biotite granite; coarse porphyritic biotite granite; migmatites; sandstones and clay; clay, limestone and siltstone. Representative samples of these rocks were sampled, taken and analysed for theheavy metals concentrations using a portable XRF of the Department of Geology Kano University of Science and

Technology, Wudil. The heavy metals determined included chromium, cadmium, lead, zinc, cobalt, nickel, copper, and manganese.

4.8.2 Chromium

Based on Taylor, (1964) the average crustal concentration of chromium is100 ppm and in the study area chromium concentration of 57.33 ppmwas obtained in ignimbrite; is far less than the crustal value; in coarse porphyritic biotite hornblende granite it averages 106 ppm,which is higher than the standard. However, Cr concentrations in the remaining analysed rock types are lower than the standard of crustal average. This means that geology does not contribute much to Cr concentrations recorded in the water sampled. However, Crcontents in the analysed water samples are higher than the water guidelines used (EPA, 2004, WHO, 2011 and NIS, 2007). It therefore means that pollution ofCr recorded is from chemical industrial pollution especially tanneries that use chromium as their raw materials.

4.8.3 Cadmium

The average crustal level of cadmium is 0.2 ppm but all rocks sampled and analysed contain Cd average values higher than the crustal value with the exception of Siltstone (table 4.21). This shows that geology is contributing factor to the high value in Cd in to water of the study area, probably in combination with other factors especially industrial, as industries in and around Kano are discharging their effluents into the nearby streams and rivers.

4.8.4 Nickel

Nickel has a crustal average of 75 ppm but its concentrations obtained in ignimbrites; coarse porphyritic biotite hornblende granite, coarse porphyritic biotite granite and migmatites are all higher than the crustal average; whereas in sandstone

and clay, clay and Limestone concentrations obtained were less than the crustal average value. Also in Siltstone a concentration of 99 ppm was recorded. It can therefore be said that the high concentration of Ni in the water may also be sourced from rocks in the area, especially when dissolved in water and with combination of anthropogenic factor especially industrial type sourced the from industries in Kano metropolis.

4.8.5 Lead

The crustal average of lead is 13 ppm.However**,** in ignimbrite and coarse porphyritic biotite hornblende granite it averages41 ppm and 234 ppm respectively. This is so probably because the rocks traversed by the waters are rich in Pb especially upstream in Ririwai. This corresponds with what was obtained by Ogunleye (2010) of about 431.6ppm in the Ririwai Younger Granite ring complex. In the remaining rock types in the study area, the concentration of Pb was more than the crustal average. Their concentrationdecreases from medium to coarse-grained biotite granite – siltstone (Table 4.19).

The trend in lead concentrations shows that the Basement granite has high lead concentration compared to lead concentrations in the rocks of the Chad Formation. This meansthat geology contributes less compared to the industrial sources especially waters from the midstream or Kano metropolis where industries are located and also where a battery smelting plant was discovered in the course of the study. In the plant waters of this industry was sampled and its concentrations was the highest and above all the standards guidelines.

The evaluated lead is a toxic element, and its high concentration exceeds the tolerance limit of most organisms.

4.8.6 Zinc

The crustal average of Zinc is 70 ppm and upstream in the ignimbrite and coarse porphyritic Biotite hornblende granite recorded values are 130 and 62 ppm respectively. Also in the coarse porphyritic biotite granite Zn contents is also higher than the crustal average with an average of 181.2 ppm. In the rest of the lithologies values are lower than crustal average with the exception of migmatites with 99 ppm higher then crustal average. However, results of Zn content in water sampled from the metropolitan Kano show higher values than in the waters from upstream (table 4.21). This means that the main sources of Zn are from industrial and domestic.

4.8.7 Copper

Copper has a crustal average of55 ppm but upstream of the study area in Ririwai39 ppm and 104 ppmwere recorded, this then shows that Cu pollution in water may probably include geological sources because of the rocks contains Cu concentrations higher than the crustal values from upstream up to the downstream of the Hadejia - Nguru wetlands and this may be in associations with other contributing factors of industrial or domestic.

4.8.8 Cobalt

In all the analysed lithologies, Co concentrations are higher than the crustal average (tables 4.19 and 4.20). This may indicate that the observed pollution of Coin the waters is also contributions from the lithological units in combinations with other sources especially in the metropolitan Kano.

4.8.9 Manganese

The crustal average of manganese is 950 ppm but all levels of concentrations on the lithologies are far less than crustal average. All the water samples analysed especially these from metropolitan Kano have higherMn concentration than the EPA 2004, NIS 2007 and WHO, 2011 recommended level. This suggests that manganese pollution is solely from industrial and domestic wastes.

Table 4.21: Heavy metals concentrations levels in rocks of the study area (ppm) KEY: Ignimbrite (JYL), Coarse Porphyritic Biotite hornblende granite (JYG), Granite (OGE) ,; Migmatite (M) ,
Sandstone and Clay (CSS), Clay (CCL), Limestone (CST), Siltstone (CLS)

Samples No.	Rock types	Names of location	Location	U	Cr	Cd	As	Ni	Pb	Zn	Cu	Co	Mn
$U6^{A}$	JYL	Shiburu	10^{0}44'36. 3''N	ND	22	36	ND	73	66	91	65	299	274
$U6^{B}$			8^{0}39'53. 5''E	ND	113	26	ND	85	26	145	140	1059	1102
U3		Zainabi	10^{0}47'44. 1''N	ND	37	32	ND	ND	31	154	107	670	647
			8^{0}45'47. 4''E										
U4	JYG	Ririwai	10^{0}43'53. 9''N	ND	ND	35	ND	93	63	261	93	325	163
			8^{0}44'35''E										
U5		Ririwai	10^{0}45'03. 8N''	ND	106	ND	ND	78	73	207	102	664	274
			8^{0}44'35. 0''E										
U7	OGE	Nata'ala	11^{0}18'12. 7''N	ND	46	37	ND	78	38	120	103	559	522
			8^{0}21'55. 3''E										
S1		Tamburawa water works	11^{0}51'07''N	ND	132	41	ND	54	37	90	49	261	202
			8^{0}30'42''E										
S2		Gadar Tamburawa	11^{0}50'33. 1N''	ND	23	24	ND	49	50	90	ND	284	359
			8^{0}30'58. 4''E										
S4		Wailari	11^{0}55'27. 4''N	ND	76	38	ND	49	50	94	54	427	349
			8^{0}32'036''E										
S3	OGP	Kwankwasiya Village	11^{0}54.02''N	ND	116	31	ND	55	42	101	59	418	285
			8^{0}31'59. 3''E										
S5		Bakin Kogi Yandanko	11^{0}52'45. 3''N	ND	83	ND	ND	60	32	110	63	480	339
			8^{0}21'01. 4''E										
S6		Yandanko Challawa	11^{0}52'45. 3''N	ND	51	27	ND	80	40	102	54	395	345
			8^{0}28'18. 2''E										

S7	OGP	Sabuwar Gandu	$11^0$57’24. 4’’N $8^0$30’45. 8’’E	ND	123	52	11	ND	1	99	143	2809	288
S8		Tatsawarki	$11^0$53’30. 6’’N $8^0$31’18. 6’’E	ND	18	27	11	102	28	82	67	203	173
U1[A]	M	Tiga dam	$11^0$27’52. 0’’N	ND	ND	28	ND	74	47	64	41	133	105
U1[B]			$8^0$24’23. 2’’E	ND	24	ND	ND	116	35	116	77	523	800
U8[A]		Chiromawa	$11^0$37’50’’N	ND	22	25	ND	ND	32	121	28	423	725
U8[B]		Kwari	$8^0$21’53. 3’’E	ND	3	32	ND	57	32	113	70	510	702
U2	M	Chiromawa Gada	$10^0$24’40. 7’N $8^0$22’42. 7’’E	ND	ND	ND	ND	69	49	60	ND	130	193
U9		Dinka Kura	$11^0$48’18. 3’N $8^0$24’16. 0’’E	ND	33	ND	ND	101	46	76	130	244	23
D1	CSS	Balare	$12^0$00’02’N $8^0$53’28. 0’’E	ND	23	27	ND	65	17	50	66	169	190
D2		Gadar Majiawa	$12^0$07’35. 0’N $9^0$10’07. 4’’E	ND	28	28	ND	83	28	39	50	142	196
D4		Hadiyau	$12^0$12’58. 2’N $9^0$51’12. 8’’E	ND	51	23	ND	76	26	47	57	368	268
D7		Hadejia	$12^0$26’26. 2’N $10^0$01’48. 3’’E	ND	42	39	ND	71	35	54	68	446	317
D3	CCI	Dungaree	$12^0$26’26. 2’N $9^0$49’27. 5’’E	ND	33	23	ND	60	27	65	56	355	331
D5	CLS	Turabu	$12^0$38’11. 0’N $10^0$09’46. 7’’E	ND	29	29	ND	71	23	40	54	286	320
D6		Marma	$12^0$38’11. 0’N	ND	41	42	ND	58	29	59	80	707	259

			$10^0$18’15. 7’’E										
D8	CST	Tsakuwawa	$12^0$11’06. 1’N $9^0$51’37. 4’’E	ND	ND	ND	ND	99	15	31	ND	65	41

Table 4.22 Average of Heavy metals concentration levels obtained from all the analysed rock from Upstream,Midstream and Downstream (Water in ppb and rocks concentrations in ppm).
KEY: Ignimbrite (JYL), Coarse Porphyritic Biotite hornblende granite (JYG), Granite (OGE), Migmatite (M), Sandstone and Clay (CSS), Clay (CCL), Limestone (CST), Siltstone (CLS)

Metals	Water	JYL	JYG	OGE	OGP	M	CSS	CCL	CLS	CST
Cr	1.75	57.33	106	69.25	78.2	28	36	33	35	0
Cd	0.21	31.33	35	35	34.25	28.33	29.25	23	35.5	0
Ni	7.37	79	85.5	57.5	148.5	83.4	73.75	60	64.5	99
Zn	29.82	41	62	98.5	34.6	40.2	26.5	27	26	15
Co	115.03	130	234	43.75	181.2	91.66	47.5	65	45	31
Cu	37.62	104	39	51.5	77.2	69.2	60.25	56	67	0
Pb	2.26	676	494.5	382.75	861	327.2	281.25	355	456.5	65
MN	405.88	674.33	218.5	358	280	424.66	294.75	331	289.5	41

4.9Stream Sediments Concentration Levels of Heavy Metals Obtained from Kano River

Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of body of water (Davies and Abowei, 2009). The erosion of bedrock and soils leads to accumulation of sediments of past or on going natural and anthropogenic processes and components. Data from sediments can provide information on the impact of distant human activity on the wider ecosystem. The composition of sediment sequences provides the best natural archives of recent environmental changes (Fagbote and Olanipekun, 2010).

Rocks samples from upstream show high concentration levels in lead, zinc and chromium and this can be related to the geology of the area where Sn- Nb – Pb – Zn – Cu mineralization is a well known feature of the Ririwai Younger Granite Complex.

Results shows that Cr has mean concentration of 61.10 mg/kg and a range from 378.20 to 5.01 mg/kg. Co has mean concentration level of 7.61 mg/kg and ranges from 20.40 to 4.05mg/kg.Ni has mean concentrations of 9.51 mg/kg with range from 17.72 to 9.00 mg/kg. Zn is with mean concentrations level of 20.80 mg/kg and ranges from 33.80 - 5.30 mg/kg. Cu has mean concentration levels of 16.01 mg/kg and with range from 36.65 to 6.61 mg/kg. Pb has mean concentration levels of 19.92 mg/kg with ranges between 45.76 to 7.40 mg/kg.Mn has mean concentration levels of 249.61 mg/kg with range between 484.76 to 147.7 mg/kg. As has mean concentrations of less than 2 mg/kg and Cd also with concentration less than 1 (Table 4.23).

All levels obtained are higher in mean and has been reported that mobility of heavy metals depends not only on the total concentration in soil and sediments but also on soil and sediments properties, metals properties and environmental factors. Highest concentrations level from upstream to downstream. Four samples from urban Kano River called metropolis where industrial and household effluents are discharged. (Table4.13). Levels obtained from the analysis were compared with values recommended in consensus based sediments quality

of Wisconsin (CBSQG), Wisconsin Department of Natural Resources, 2003 as shown in table 4.23. The CBSQG is applied to biologically active zone associated with deposit sediments flowing (streams and rivers) and even static (lakes and ponds) water bodies and wetland soils and sediments.

Samples of sediments taken along the Drainage Basin from upstream to the downstream are all wet type and saturated. Concentrations obtained shows that it is almost as the same with one in the groundwater.Reason for this is that there may be no any absorption by sexquioxides soils in the processof water infiltration in to the ground. This means that water will pass in to the ground to recharge groundwater with out any absorption by the sediments. Also most tube wells, wash bores and boreholes were drilled within the river, and are the major sources of water to Kano metropolis and Wudil.

Table 4.23 Showing the Concentration Levels of Heavy Metals in Sediments of Kano River

	Lat.	Long.	Name of Sampling Point	Cr	Co	Ni	Zn	C u	As	Pb	Cd	Mn
Rocks	**10.71694**	**8.744722**	**Ririwai**	**28.50**	**4.5**	**8.01**	**28.05**	**11.56**	**<2**	**29.00**	**<1**	**147.7**
Samples	**10.79528**	**8.768056**	**Zainabi**	**5.01**	**8.39**	**8.65**	**22.69**	**12.01**	**<2**	**13.41**	**<1**	**184.7**
Sediments	**10.71694**	**8.744722**	**Nataala**	**16.69**	**4.05**	**9.19**	**26.15**	**9.47**	**<2**	**7.37**	**<1**	**210.53**
Samples in water	**11.29639**	**8.599722**	**KwariChiromawa**	**24.44**	**-**	**8.93**	**11.63**	**23.94**	**<2**	**21.32**	**<1**	**242.27**
	12.51111	**10.16278**	**Kano River**	**28.98**	**4.74**	**7.94**	**5.29**	**19.98**	**<2**	**45.76**	**<1**	**217.13**
	11.62472	**8.360833**	**Tatsawarki**	**142.29**	**8.91**	**8.64**	**33.78**	**7.63**	**<2**	**17.01**	**<1**	**184.27**
	12.36528	**9.92**	**Wailari**	**378.18**	**20.36**	**17.72**	**11.24**	**32.15**	**<2**	**23.14**	**<1**	**484.14**
	11.92361	**8.535278**	**Yandanko**	**5.83**	**6.79**	**8.68**	**29.05**	**8.65**	**<2**	**14.52**	**<1**	**197.38**
	12.13417	**9.164167**	**Wudil**	**47.12**	**7.91**	**8.58**	**26.85**	**9.88**	**<2**	**13.72**	**<1**	**181.73**
	11.87944	**8.4725**	**Majiyawa**	**6.03**	**7.85**	**9.03**	**11.22**	**36.65**	**<2**	**21.31**	**<1**	**219.61**
	10.79528	**8.768056**	**Hadiyau**	**32.04**	**5.9**	**9.63**	**22.6**	**6.61**	**<2**	**10.94**	**<1**	**484.7**
	11.88167	**8.522778**	**Turabu**	**17.98**	**4.34**	**9.13**	**21.08**	**13.6**	**<2**	**21.52**	**<1**	**241.21**
	Average			**61.09**	**7.61**	**9.51**	**20.80**	**16.010**		**19.918**		**249.61**
	Maximum			**378.18**	**20.36**	**17.72**	**33.78**	**36.65**		**45.76**		**484.7**
	Minimum			**5.01**	**4.05**	**7.94**	**5.29**	**6.61**		**7.37**		**147.7**

Table 4.24 Comparison of Concentrations of Heavy Metals in Sediments in the Study Area With International Guideline of Consensus Based Sediments Quality of Wisconsin

Metals	Average of the Study Area (mg/kg)	Netherlands (CBSQG) guidelines (mg/kg)	Remarks
Sb	-	2	
As	<2	9.8	
Cd	<1	0.99	EQUAL
Cr	61.10	43	High
Cu	16.01	32	Low
Fe	-	2000	-
Pb	19	36	Lower
Hg	249.61	460	Less but more than half
Mercury	-	0.18	-
Ni	9.52	23	Less
Ag	-	1.6	-
Zn	20	120	Less

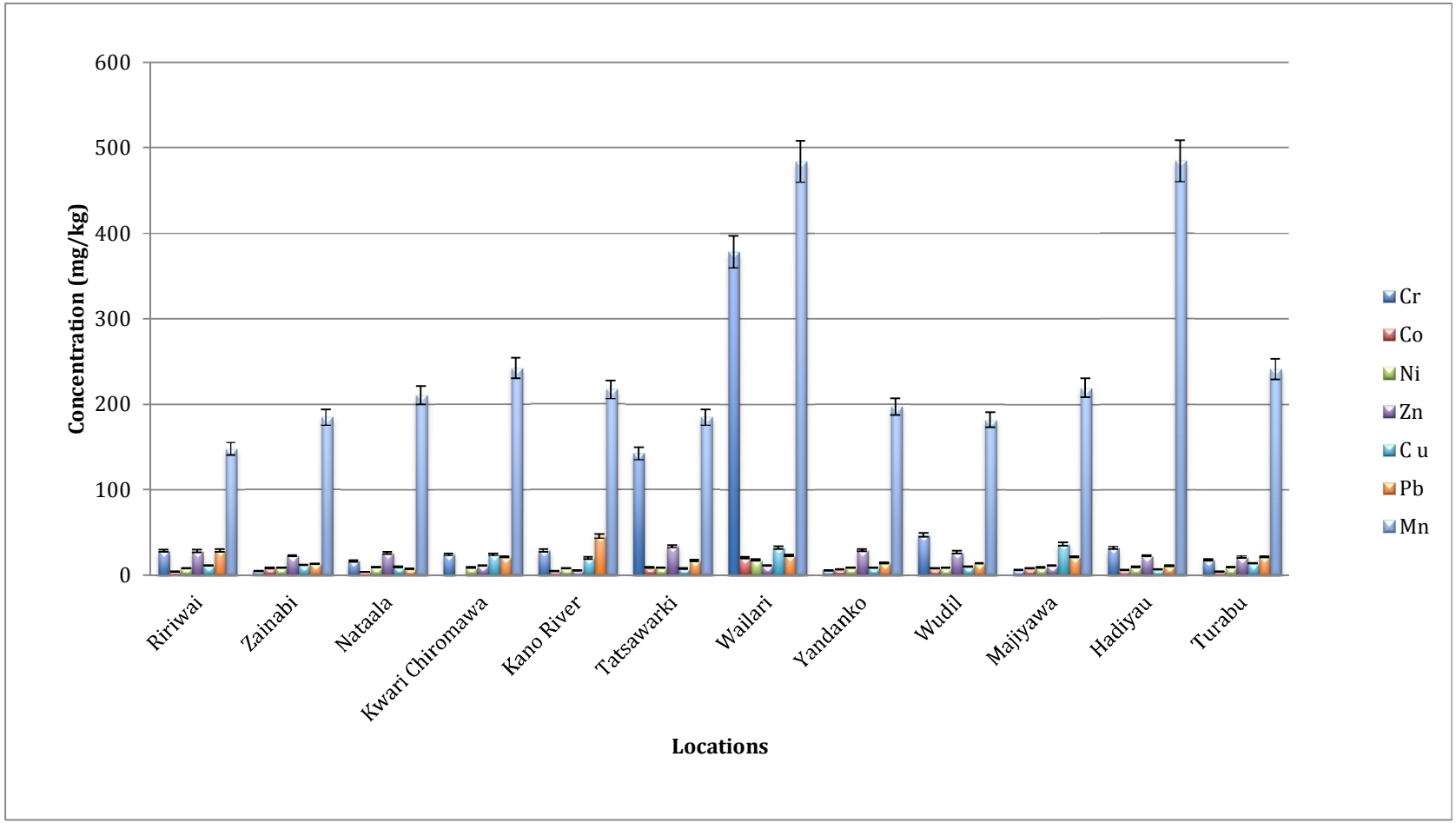


Figure 36. Heavy Metals Concentration in Solid Rocks and in Sediments (Alluvium) of the Kano River Drainage Basin. See table 4.22 where coordinates of sampling points and numerical values

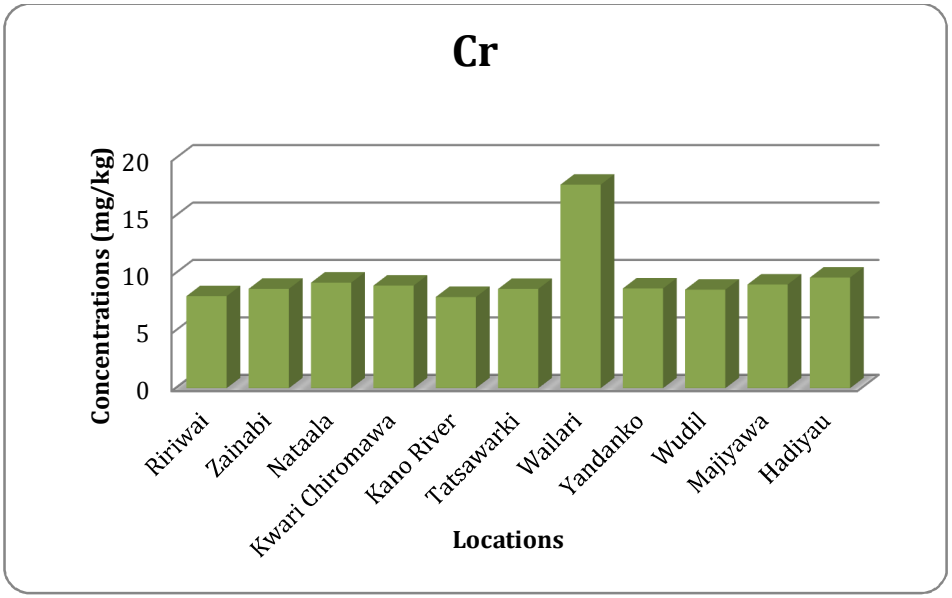


Figure 37 . Concentrations of chromium in rocks and alluvium sediments from upstream to the downstream of Kano River. Highest concentrations of Cr in Wailari part of Kano Metropolis. (See table 4.21 where coordinates of sampling points and numerical values are shown

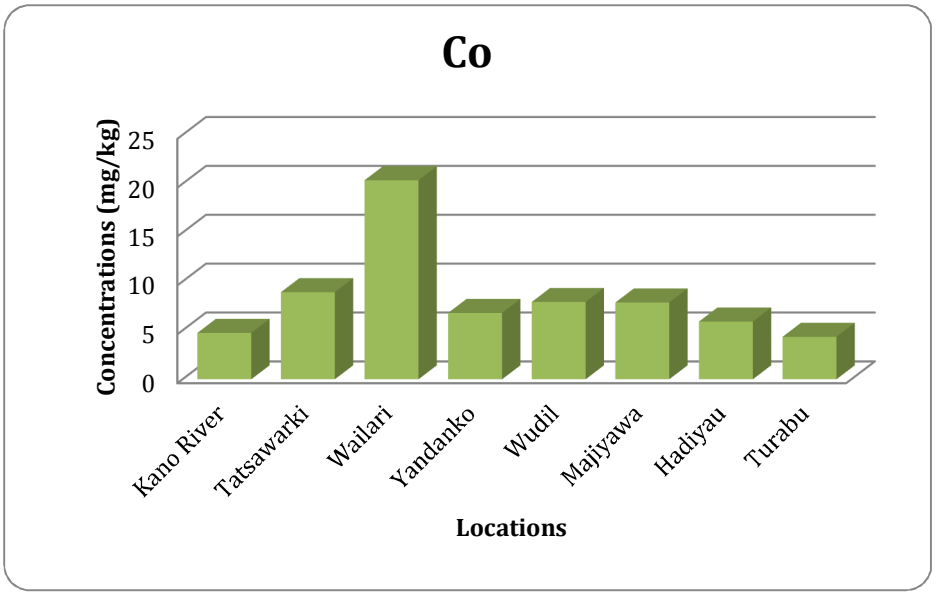


Figure 38. Concentrations of cobalt in rocks and alluvium sediments from upstream to the downstream of Kano River. Highest concentrations of Cobalt in Wailari part of Kano Metropolis. See table 4.21 where coordinates of sampling points and numerical values are shown.

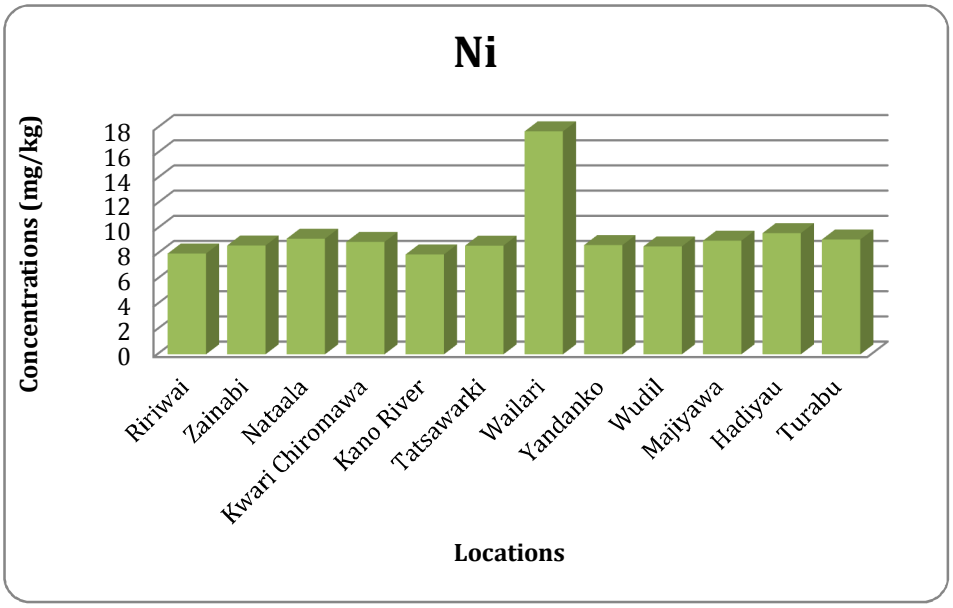


Figure 39. Concentrations of nickel in rocks and alluvium sediments from upstream to the downstream of Kano River. Highest concentration of Ni in sediments from Wailari Kano Metropolis. (See table 21 where coordinates of sampling points and numerical values are shown)

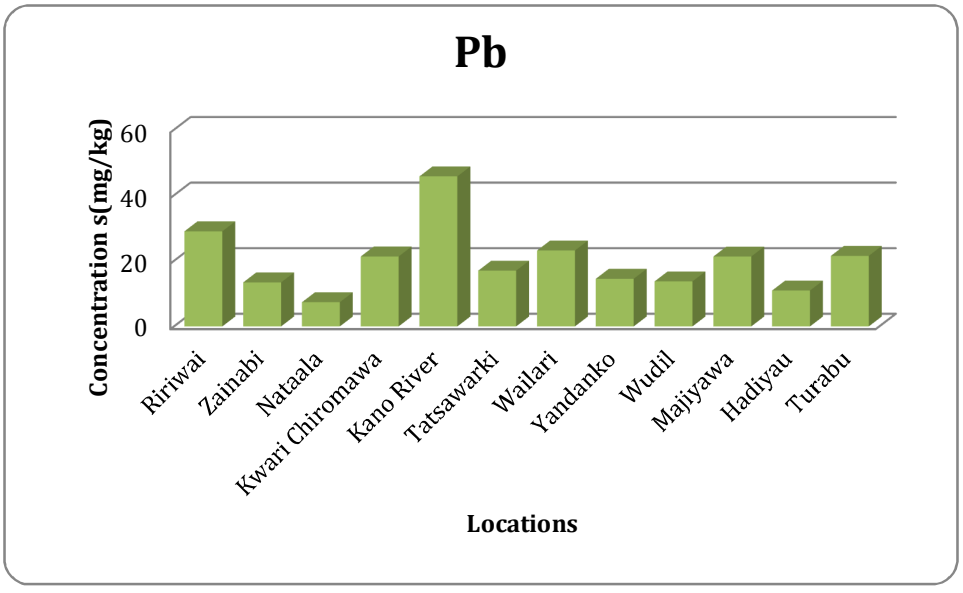


Figure 40. Concentrations of Lead in rocks and alluvium sediments from upstream to the downstream of Kano River part of Kano Metropolis. See table 4.21 where coordinates of sampling points and numerical values are shown

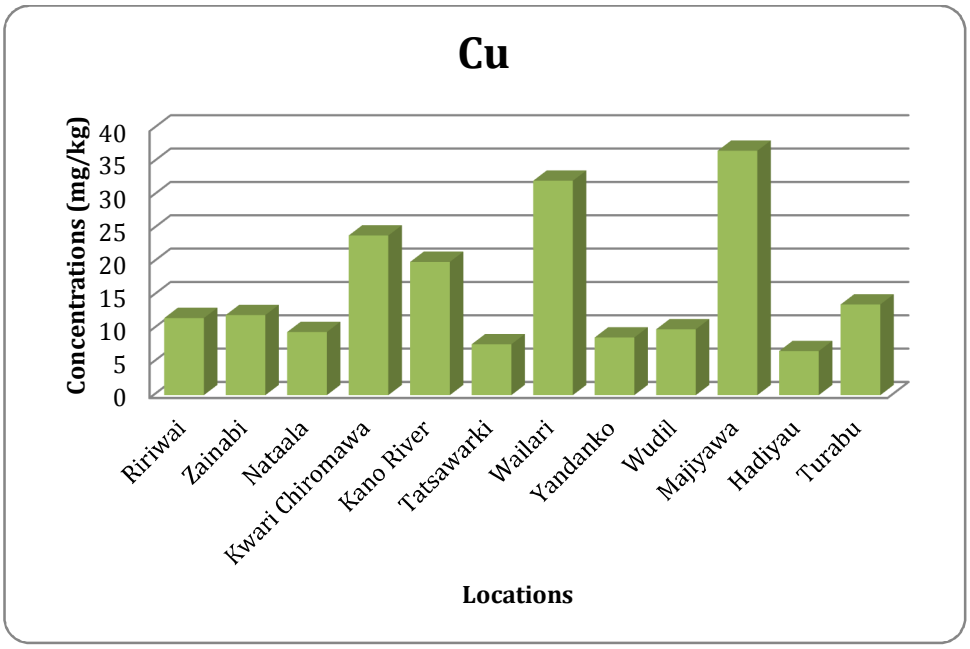


Figure 41. Concentrations of cupper in rocks and alluvium sediments from upstream to the downstream of Kano River. Highest is downstream at Majiawa but then in Wailari and upstream Chiromawa. See table 4.21 where coordinates of sampling points and numerical values are shown

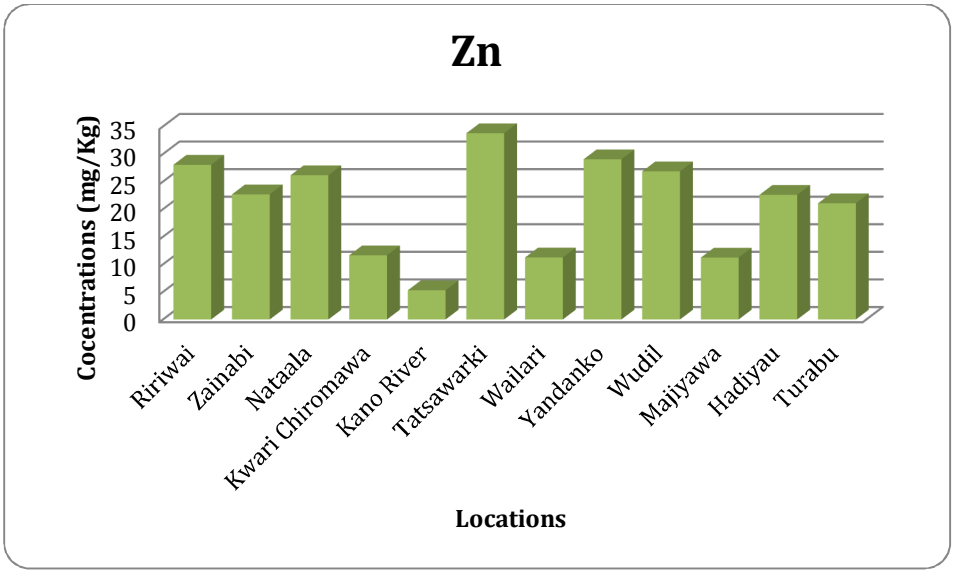


Figure 42. Concentrations of zinc in rocks and alluvium sediments from upstream to the downstream of Kano River. Highest concentration of Zn in Ririwai and Wailari in Kano metropolis See table 4.21 where coordinates of sampling points and numerical values are shown.

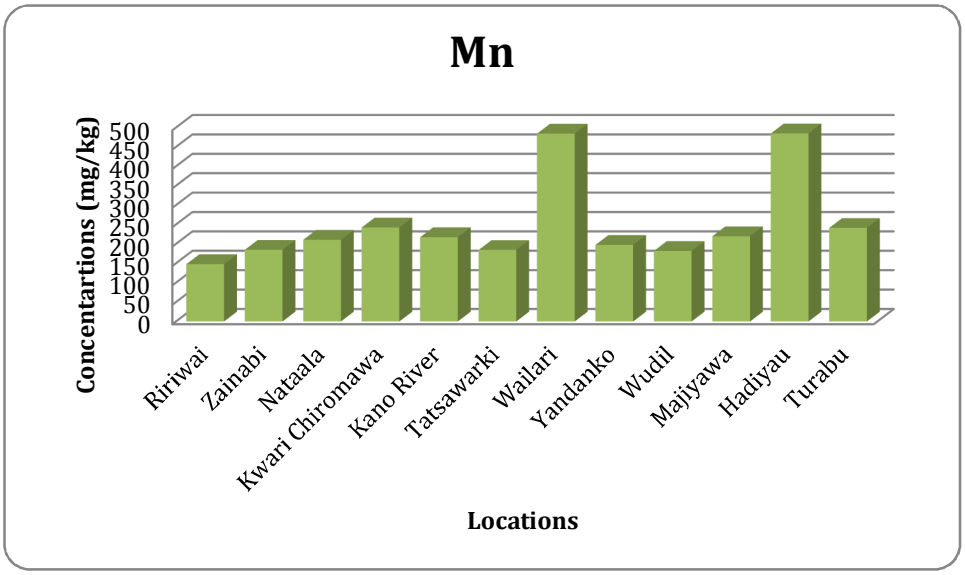


Figure 43. Concentrations of manganese obtained in rocks and sediments from upstream up to the downstream of Kano River. See table 4.21 where coordinates of sampling points and numerical values are shown.

4.10Evaluation on Organic Carbon, Inorganic Carbon and Total Carbon in Water (surface and groundwater)

The determination of total organic carbon is an essential part of any site characterization or ecological assessment since its presence or absence can markedly influence how chemicals will react in the soil or sediment or in water. Carbon can be present in elemental, inorganic, or organic forms. Carbon is usually derived from weathering of the parent material/geology, the decomposition of plant and animal matter, or by addition through anthropogenic activities.Organic matter in water, soils and sediments is widely distributed over the earth surface occurring in almost all terrestrial and aquatic environments (Schnitzer, 1978).

Beside the natural process there are human inputs that contribute to the organic matter in water. These include large volumes of poorly defined wastes, such as domestic sewage or pulp mill effluent that are sometimes discharged directly or

after treatment into rivers, lakes, and oceans. Besides the bulk effluents, anthropogenic sources also supply specific organic compounds, agricultural chemicals, medicinal, and products or by products of industrial processes.

It will be interesting here to define these terms and their usefulness in water quality studies. Organic carbon is deposition formed from biological process such as organic matter that adds nitrogen into soil in form of NH_4 - $N0_3$. Inorganic carbon is the chemical process or chemical contents in water that comes from minerals usually fertilizer like NPK, SSP etc. Total organic carbon is the sum total of all organic in soil or water that are not readily dissolved or decomposed (Plants and animal residue) that is not ready to be used by plants.

In the study area this was tested in the water samples from upstream to downstream and results obtained shows that total organic carbon in water is higher than standard of useof water for medicinal use especially water for medicine and injections. This is more and this is much more in surface water. Surface water is flowing especially in metropolis from discharges from industries. In contrast to spilled contaminants, in various sites observed in the field the flowing water contains discrete organic carbon bearing particles such as wood fibres possibly from pulp mill waste or leather scraps from tanneries waste. At these locations the total carbon contents contributions to these waste is significant to a domination fraction of TC determined for all the samples ranges from 348.48 to 0.09 ppm with an average of 41.07 ppm.

Also inorganic carbon ranges from 982.46 to 0.09 ppm with average for the study area of 28.07 ppm.TOC in water ranges from 188 to 0.25ppm and average of 13 ppm.

Table 4.25 Results of total carbon, organic carbon and inorganic Carbon contents in water from the Kano River Drainage Basin

Customer Description	Lab. Description	Total Carbon (ppm)	Inorganic Carbon (ppm)	Total Organic Carbon (ppm)
01A	173/P2/12	27.39	22.92	4.47
02A	174/P2/12	10.00	6.00	4.00
03A	175/P2/12	28.03	23.53	4.50
04A	176/P2/12	29.58	27.49	2.09
05A	177/P2/12	29.60	25.36	4.24
06A	178/P2/12	17.08	15.97	1.11
07A	179/P2/12	14.89	13.50	1.39
08A	180/P2/12	11.62	8.00	3.00
09A	181/P2/12	12.12	9.00	3.00
10A	1182/P2/12	10.10	9.0	1.00
11A	183/P2/12	21.73	17.86	3.87
12A	184/P2/12	27.25	25.33	1.92
13A	185/P2/12	14.04	10.00	4.00
14A	186/P2/12	1.53	9.00	5.00
15A	187/P2/12	19.05	17.64	141
16A	188/P2/12	14.81	10.0	5.00
17A	189/P2/12	21.04	19.48	1.56
8A	190/P2/12	17.85	15.97	1.88
19A	191/P2/12	15.87	10.6	5.25
20A	192/P2/12	12.98	8.00	5.0
21A	193/P2/12	348.48	160.28	188.20
22A	194/P2/12	20196	99.52	102.44
23A	195/P2/12	32.28	28.75	3.53

24A	196/P2/12	13.15	11.04	2.11
25A	197/P2/12	41.44	38.07	3.37
26A	198/P2/12	16.43	14.60	1.83
27A	199/P2/12	25.6	22.14	3.48
28A	200/P2/12	68.43	64.1	4.25
29A	201/P2/12	-	-	-
30A	202/P2/12	18.89	16.50	2.39
31A	203/P2/12	30.31	23.15	7.16
32A	204/P2/12	33.67	29.41	4.26
33A	205/P2/12	50.72	47.47	3.25
34A	206/P2/12	139	106.20	32.80
35A	207/P2/12	19.02	17.60	1.42
Uncertainty		9%	9%	25%
Sum		1,389	982.46	421
Average		41.40	28.07	13
Maximum		348.48	982.463	188
Minimum		0.09	0.09	0.25

CHAPTER FIVE

5. CONCLUSIONS, CONTRIBUTIONS AND RECOMMENDATIONS

5.1 Conclusions

Various parameters determined from both field and laboratory analysis of groundwater and surface water samples from upper, middle and lower course of the River Kano drainage basin were used to define and characterised the background levels of heavy metals and other elements and the extent of their pollution.

The upstream part is represented by the highlands of the Ririwai younger Granites Complex, the Pan-African basement granites and gneisses and the anthropogenic influence of the Kano metropolis dominate the Midstream.

Elements concentrations in sediments and rocks were compared with CSBQ, which showed that the sediments are high with much concentration in the heavy metals especially being wet.

This means the water is polluted and may affect the groundwater level due to lack of absorption by soils and sediments during infiltration to groundwater. This then means that what is obtainable in the groundwater is same as surface as well as sediments so the water is generally polluted especially in Kano metropolis where wash bores and boreholes are feeding the Kano populace (Tamburawa as well as Wudil area one of the water regional schemes in Kano State.

High heavy metals values show that water from Kano metropolis (both ground and surface water) is heavily polluted and extent of pollution has reached most parts of the downstream of the drainage basin where it is being used most for domestic and

irrigation purposes. A battery recycling company was found to be contributing to Pband Cdpollution of both surface and ground water.

Based on major ion pollution (cations and anions) levels obtained and compared with standards show that the water can be used for both domestic and irrigation i.e. in general terms from upstream midstream and downstream.

Concentrations levels in heavy metals was also determined from upstream up to the downstream and from results obtained show that some rocks also contributes to the pollution especially in upstream in terms of Cd, Mn, Pb and Ni and Co this was compared with crustal average.

5.2 Contributions

This work contributed knowledge in the following ways:

1. Finding levels of concentrations in heavy metals from upstream, midstream (Kano Metropolis) and its downstream Hadejia-Nguru wetlands in both surface and groundwater. It was found that the water from upstream both surface and groundwater generally non polluted with exception of one in Ririwai which has much of the heavy metals but this is based from the geological background of the area. Also for midstream water, which is highly polluted and cannot be used based on levels of concentrations obtained. Downstream is alsopolluted especially surface and so doubtful on its usage.

2. Finding levels of major ions concentration in water both surface water and groundwater from upstream up to downstream of the Kano river drainage basin. And found that the pollution in this generally non polluted especially upstream but in midstream is tolerable as well as downstream

3. Findings level of concentration in rocks as background based on the geology as well as in sediments from upstream up to the downstream of the drainage basin. Based on sediments the y is highly rich in these metals. It therefore means that sediments do not absorb metals in the process of infiltration into the ground. Therefore, this means surface water that passes in the river from midstream infiltrates and recharges the groundwater with these levels it contained in heavy metals.

4. Comparing level obtained in all above with guideline and standard to qualify water for various forms of uses within the river drainage basin based on the sampling category as either upstream midstream or downstream.

5. Determining the extent to which levels of pollution from midstream has reached upto the downstream in both surface and groundwater and was found that pollution especially in surface water has reached most parts downstream based on the levels of concentrations obtained from the results of analysis.

6. Finding a greater water polluter in the study area a battery recycling company that is a major polluter of water of lead.

In all above the work has contributed in determining the levels of concentrations in water of both heavy metals and major ions from both groundwater and surface water. It also contributed in finding levels of concentrations in rocks and sediments from upstream up to the downstream and compared with standards as well as ascertained the contributions of lithological units in polluting the water (surface and groundwater). Extent to which pollution has reached from midstream to downstream was also determined in both surface water and groundwater. Levels of organic, inorganic and total organic carbon contents in both surface and groundwater were also determined which is very essential in pharmaceutical companies especially

in drugs manufacturing and water for injections. This work will help and be useful in planning and management of water resources of the study area as well as environmental hazards associated with water. This work will also be tempting if further research will be taken and compared with this on the prevalence of carcinogenic diseases that are at increase especially in the metropolitan Kano and downstream.

5.3 Recommendations

This study evaluated levels of concentrations in heavy metals, major ions in water as well as in rocks and sediments within the Kano river drainage basin. Locations with elevated level were also mapped. Its health impact on humans was also discussed. So it will be interesting here to recommend further studies in the drainage basin as follows:

1. Need to finding levels of heavy metals concentrations in sediments especially in the metropolis and downstream in order to determine the mobility in water.

2. Further research is needed on this to also determine concentration levels of heavy metals in various organs of aquatic animals in the study area from upstream midstream and downstream.

3. Further research to find levels of heavy metals in both groundwater and surface water especially in the Kano metropolis with special preference to water from Tamburawa and Wudil where greater percentage of the populace uses for both domestic and irrigation.

4. Need to find the bio magnifications in crops watered with this water from midstream upto the downstream on levels of heavy metals since they are never remobilised plants absorbs them and man eats these crops grown with these waters.

REFERENCES.

Abaa, S. I. (1976): The Geochemistry, Petrology and Mineralisation at Ririwai,Gindi Akwati and Dutsen Wai in Nigerian Younger Granite province. Unpublished M.Sc. Thesis, Ahmadu Bello University, Zaria. pp.16-50

Adegoreye, G. (1997): Environmental Consideration in Properly Design Urban development and Renewal. In AkinjideOsonkugan (Ed). *Dimension of Environmental Problems in Nigeria*. Pp12-25

Agriculture and Natural Resources Department (1993): Agricultural Extension Report KUM/NRD/1/55.

AhmedK. and Tanko A.I. (1994):Assessment of Water Quality Change for Irrigation in River Hadejia Central Catchment. *Journal of Arid Agriculture* Vol. 10, pp89-94

Ayers, R.S. and Westcot, D.W.(1985):*Water Quality for Agriculture*.FAO publication. United Nation, Rome, Italy. 97pp

Bala, M., Shehu, R.A. and Lawal, M. (2008): Determination of the level of some heavy metals in water collected from two pollution- prone areas around Kano Metropolis. Bayero Journal of Pure and Applied Sciences (BAJOPAS) Vol. 1 No. 1 December 2008.

Bichi, M.H. (2000): Surface water quality in Kano industrial environment. In Falola, J. A. K. Ahmed, M.A. Liman and A. Maiwada (Eds) *Issues in land Administration and Development inNorthern Nigeria* Department of Geography, Bayero University Kano, and pp 305-313.

Binns, T. Maconachie, R. and Tanko, A.I. (2003): Water, land and health in urban and Peri-urban Food Production: the case of Kano, *Nigeria Journal of Land Degradation and Development. 14; 431-444*

Boboye, O. A. (2008): Hydro Chemical Assessment of Groundwater in Iddoh area, Southern Nigeria.Journal of Mining and Geology. Vol. 44. NO.2

Brian, M. (1966): *Principles of Geochemistry*. John Wiley and sons. New York

Buchanan and Pugh (1983): International Water technology Conference and Exposition (AUGA Expo 83) Acapulco, Mexico

Buerman, Y. Du Prez, H.H. Steyn G.J. Deacon, A. (1995): Suspended silt concentrations in the lower Olifants River (Mnumalanga) and impacts of silts releases from the Phalabowora Barrage on water quality and fish survival. Koede. 38 pp 11-34.

Clayton, J.L. (1979): Nutrient supply to soil by rock weathering. Occasional paper, state University, Syracuse, pp75-96

Dahiru, M. (1989): Some Heavy Metals in Plant Irrigated Water with Sewage Effluent of ABU Stabilization Pond. Unpub. Msc. Thesis, Dept. ofWater Resources Engineering. A.B.U Zaria.

Daily Trust, (2008): *Pollution turns Chinese river red*. Daily trust newspaper. Feb. 29th 2008.

Davies, T.C. (1994): Water Quality Characteristics Associated with Fluoride Mining in Kerio valley Area of Western Kenya. *International Journal of Environmental Health Research* Vol. 4 pp. 165-175

Davies, O. A. and Abowei, J. F. N. (2009): Sediment quality of lower reaches of Okpoka Creek, Niger Delta, Nigeria. *European Journal of Scientific Research*26(3): 437 - 442

Donneen L.D. (1949): The Quality of Irrigation Water and Soil Permeability. *Soil Science. American Proceedings. Vol 13, pp 526.*

Don-Pedro, K.N. Oyewo, E.O. Otittolujo,A.A. (2004): rend of heavy metal concentrations in Lagos lagoon ecosystem, Nigeria. *West Afr. Journal of Applied Ecolgy.5 pp103-114.*

Du Preez and Richards, (1958): The Hydrology of Gumel Emirate, Kano province Record of GSN, 1955. Pp59-64.

Durov, S.A. (1948): Classification of Natural Waters and Graphic Representation of their Composition, Doklady. 59(1): 87-90

Ejechi, B.O. and Odun, O (1996): *An investigation into the Event of Pollution of Some Nigeria's rivers*. A Report submitted to Nigerian Environmental Study / Action Team.

EPA (2004): Human Health Fact Sheet, Argonne national Laboratory, US, pp 17

EPA (2000): National Primary Drinking Water Regulations; Radionuclides. United State Environmental protection Agency (EPA). Final Rule, pp 231

Ewulu, P. (1983): Effects of Pollution Discharge on Kaduna River Water Quality. Unpublished. M.sc. Thesis Dept. of Chemistry, ABU Zaria.

F.A.O. (1985): *Water Quality for Agriculture. Irrigation and Drain*age.Paper No. 29 (Rev. 1) F.A.O. Rome. pp1-174.

Faboya, O.O.P. (1997): *Industrial Pollution and Waste Management*. In AkinjideOsunkugun (Ed). Dimension of Environmental Problem in Nigeria pp 26-35.

Fagbote E. O.andOlanipekun E. O. (2010): Evaluation of the Status of Heavy Metal Pollution of Sediment of Agbabu Bitumen Deposit Area, Nigeria**.** *European Journal of Scientific Research* Vol.41 No.3I pp.373-382

Federal Environmental Protection Agency (FEPA) (1990): Proposed National Guidelines for Effluents Limitations, gaseous Emissions, and Hazardous Solid Wastes Management for Industries in Nigeria. FEPA, Nigeria.

Federal Ministry of Environment, (2001): Studies for Industrial Effluent Treatment Facilities in Kano. *A preliminary report*. Report prepared by MAP Industrial and Environmental Audit and GMBH Germany.

F.A.O. (1985) : *Water Quality for Agriculture*. Irrigation and Drainage.Paper No. 29 (Rev. 1) F.A.O. Rome pp1-174.

Htt: www.brad.ac.uk/acad/ensci/ET/glossary/enviglas.htm

Garba, L.M.(2000): Lead (Pb) Concentration in the Water of Kubanni River Dam, Zaria. Unpub. M.Sc. Thesis. Departmentof Geology, ABU Zaria.

Garba, I. (2005): Hydrogeology ofKabo Topographical Sheet 80 NW 1: 50,000 Unpublished. M.Sc. Thesis. Departmentof Geology ABU Zaria.

Greenland, D.J. and Hayes, M.H.B. (Eds. 1981): The Chemistry of Soil Processes. John Willy and Sons ltd. Pp. 593-610.

Hilgard, E. W. (1960): Soils, their formation, properties, composition and relation to climate and plant growth. Macmillan, New York.

Ironsi, A. L (1988): "*A world under sword*" News watch, Lagos, Vol. 10/8 No 3 pp. 14-15.

Isa, M. (1984); Hydraulic Properties of Aquifers in Kano State. Unpublished M.Sc thesis. Department of Geology, Ahmadu Bello University, Zaria, Nigeria.

Iskander, I.K. (1975): Urban Waste as a source of Heavy Metals in land treatment. Paper presented at the International Conference on Heavy Metals in the Environment Toronto Canada. In Drinking Water Quality Enhancement through source.

Jacobson, R.R.E, Mac Leod, W.N. (1977): Geology of the Lirue, Banke and Adjacent Younger Granite Ring- Complexes. Geological Survey of Nigeria Bulletin No. 33

Jones, M. J. (1985): The Weathered Zone Aquifers of the Basement Complex Areas of Africa *Q.J Eng. Geol.18* pp. 35-46

Kabiru, A.(2010):The Kano Physical Environment. http://www.kanoonline.com/sponsordedby Kano Forum. Kano Nigeria

Kano State Water Board (2000): Greater Kano water Supply Feasibility Study. Unpub.

Kasuya, M Tarnish, H. Aosima, K. Katoh, T. Podjack R.B. Eds.Annabor Science Publication.Hongudi, T. Morikawa Y. Nisty O.M. and Iwata K (1992): Water pollution by Cadmium and the onset of Itai-itai disease in Matsui (Ed) hazard assessment and Control of Environmental Contaminants in water vol. 25 No.11. 1992 ISS No.273-112.

Khan, H. U. (1981): Industries Waste Characteristics in Anambra State, Nigeria. Unpub. Reprt to Anambra State Government.

KNARDA (1986): Year Book Record of Work. 1983-86

Klien, L. (1992): River pollution Causes and Effects. Butterworth, London.

Leewock, C.P. (1994): Study on Use of Urban Waste By near Urban Farmers of Kano Metroplis No. OA 354 NRI UK.

Linda, G. (1974): Hydrological Effects of Urbanisation in Sweden. *Hydrological Efects of Urbanisation (Studies & Report on Hydrology)*.18 Passe, UNESCO Press.

Magdi, O. (1999): Geological and Geochemical Investigation of lateritic profile around Kano. With Special Reference to the Distribution of Base Metals (V, Cr, Mn, Co and Ni). AnUnpublished.M.Sc Thesis Department of Geology, ABU, Zaria.

MC Curry, (1973): Geology of. the Precambrian to lower Palaeozoic rocks of Northern Nigeria. A Review. In C.E. Kogbe (ed).*Geology of Nigeria*. Elizabeth Publishing Company, Lagos pp15-39

Ministry of Environment (1999): National Guidelines and Standards for Water Quality in Nigeria

Mummy, G.E. (1970) "*Law private property and environment* "A Provocation to a debate onthe problems of environmental pollution.

Musa, L. (1997): The effects of Industrial growth on metropolitan Kano. Unpublished. B.Sc. Project Department of Geography, BUK, Kano.

NAFDAC (2000): Standard Guideline For Water. Unpublished

Nigerian Geological Survey Agency (2006): Geological and Minerals Maps of Kano and Jigawa States.1: 100,000. 2004 Edition.Nigeria.

Nigerian Industrial Standard, 2007 (NIS): *Nigerian Standard for Drinking Water Quality*, NIS 544:2007. Approved by Standard Organisation of Nigeria, ICS 13,060.20,30pp

Nwadiokwere,C.L. and Ezihe, C.A. (1990): Environment International, Vol. 16, pp295-305

Nwanko, C.C. (1987) Pollution Studies in Nigerian Rivers Heavy Metals levels of Surface Water in the city of Jos. Paper presented at the 12th Annual Conference of the Chemical society of Nigeria. Calabar 3-25th Sept. pp13.

Nwanko, C. C. and Onyeyekha, T. (1989): "Trace Metals levels In the Effluence Discharged from Industries in Jos, Kaduna and Kano Industrial Areas. A comparative study; paper presented at the *National Workshop on Waste Disposal Environmental Pollution and Community Health*.University of Ibadan.Pp13-16.

Ogbonna,J.O. Lawal, F.A.Owoeye, L.D. Udeh, U. (1998): Chemical Characteristics and Fertilizing Value of Primary Sludge from Tannery Effluent Treatment Plant. Paper presented at *16th Annual National Conference of Institute of Science & Tech. Ibadan* 24th-27th Nov. 1998

Olofin, E.A (2000): The gains and Pains of Putting a Water look on the Face of the Nigerian Dry lands. Bayero University Kano Inaugural Lecture `Series No. 1and 2 ISBN 978-2035-97-11

Olofin, E. A., Nabegu, A.B. Danbazau, A.M. (2008) *Wudil within Kano region A geographical synthesis.*

Parkman, I. (2000): *Greater Kano water supply Feasibility Study*. Final report to Kano State Water Board. Vol. 1& 3 Sept. 2000

Piper, A.M. (1944): A Graphical Procedure in Chemical Interpretation of Groundwater analysis. *Trans. American Geophysics Union*. 25:914-923

Richards, L.A. (1954): *Diagnosis and Improvements of Saline alkali Soils: Agriculture*, Vol.160.handbook 60, US department of agriculture, Washington DC. 160pp

Schnitzer, M. 1978.*Humic substances*: Chemistry and reactions. In: *Soil Organic Matter*, M. Schnitzerand S.U. Khan, Ed. Elsevier Scientific Publishing Co., New York. Pp. l-64.

Schoeneich, K. and Amusa, F. (1990): *On the Isotactic origin of the Younger Granites Isenbergs in Jos, Nigeria.* Paper presented at the Nigerian Geomorphology Working Group, 2nd Annual Seminar. The management of land degradation in Nigeria held at the Department of Geography, University of Benin, Benin City, Nigeria, 25thJanuary 1990.

Schoeneich, K. and Mbanu, W.O. (1991): *Excursion Guide Book on the Geology of Plateau and Yankari Game Reserve*. Nigerian Mining Geosciences Society 27thAnnual Conference. Jos. Published by Nigerian mining ad Geosciences society Jos chapter.

Schoeneich, K. (1998): Geol. 405 *Lecture Note Dept*. of Geology A.B.U Zaria.

Schoeneich, K. (2001): Concentration levels of Heavy metals as Pollutants on Jos Plateau. Unpublished. Research for University of Jos Plateau. Grant R.G 1993/94.

Schoeneich, K and Aku M.I. (1998): *The Study of Degraded Mineland of Jos, Bukuru, Riyom, B/Ladi and Bokkos Areas of Jos Plateau for Development Possibilities*Unpub. Project for Platue State Environmental planning and Protection Agency, Jos.

Schluter, T.,Tranth, M.H. (2008): Geological Atlas of Africa, with Notes on Stratigraphy, Tectonics, Economic Geology, Geohazards, Geoscites and geo-Scientific Education of Each Country. http;//boos.google.ca/books?/id=ifvkwpspdc$ pg=pg273

Shainberg, I. (1978): *Quality of irrigation, sanitation and environmental sustainability*: The Financing Challenge. World Bank, Washington, D.C. pp 76

Siddle R.C. and Sopper, W.E. (1976): Cadmium Distribution In Forest Ecosystem Irrigation with Treated Municipal Wastewater and sludge. *Journal of Environmental Quaility*.Vol. 4940 pp 419-422

Sokoto, A.M. (1981): Determination of some water quality in Sharada Industrial areas, Kano State, B. sc Geography Dissertation, Bayero University, Kano.

Tanko, A. I. (1997): Industrial wastewater pollution and its effects on shallow ground water sources in metropolitan Kano. Paper presented at the *40th annual Conference of the Nigerian Geographical Association. Bayero University Kano, May 4-7, 1997*.

Tanko, A. I. (2002):Spatio- Temporal Patterns of Environmental Pollution and Control in Metropolitan Kano, paper presented at the *45th Annual NGA Conference, University of Ilorin, 3th July-7th July 2002*

Tanko A. I. (2008): An overview of Industrial Effluents, Management and Effects in Kano State Nigeria. Paper presented at the stakeholders Conference on *Industrial Effluent Treatment facilities in Kano Sate*, 10-11th Nov. 2008 Kano.

Taylor,S.R. (1964):Abundance of Chemical Elements in the Continental Crust: a new table. Geochem. Cosmochim.Acta28, pp1273-1285

Tijjani, M.N. Jinno, K. and Horoshiro, Y. (2004): Environmental Impacts of Heavy Metals Distributions in Water and Sediments of Ogunpa River, Ibadan area, southwestern Nigeria

Tudunwada, I.Y. (2006): Effects of Some Soil Amendment Concentrations in Sorghum and Millet in the Soils of Challawa Industrial Area Kano State. Unpub. Ph.D Thesis Dept. of Geography B.U.K. Kano.

Tukura, B.W.,Kagbu, J.A. and Gimba, C.E.(2005): Bioaccumulation of Trace metals in Fish From Ahmadu Bello University Dam. *Nigerian Journal of Scientific Research.*A B U Zaria Vol. 5 No. 1 pp. 91-95

Udoh, A. P. Omenesa, H. Z. and Sing, K. (1987): Determination of Some Quality Assessing Parameters for Drinking Water in Zaria. *Nigerian Journal of Scientific Research.*A B U Zaria Vol! No. 1 pp53-56

Van der Merwe, M., Van Vuren J.H. Du Preez, H.H (1993): Lethal Copper Concentration Levels for Clarias - Gariepenus (Burchell, 1822)-(A) *Preliminary study*. K.O. Ed. 36 pp 77-86.

Wardley- Smith,J. (1983): The Control of Oil Pollution: Graham and Trotrian Publishers.

Wetzel, R.G. (2001): Limnology. Lake and River Ecosystems. Academic London. P 1006

World Bank (1995); Nigeria Strategic Options for Redressing Industrial Pollution Vol. 1 Feb.3 1995. Enterprise Development and Public Sector Management Division West Central Africa Department, Washington D.C.

Water Resource Institute (1988): Report on the Hydrological Characteristics of Three River Basins in the Sudano- Sahelian Zone in Nigeria. Unpub.

WHO (2004): *Guidelines for drinking water quality*, Volume 1. World Health Organisation, Geneva. Pl-494

WHO (2011): *Guidelines for Drinking Water Quality,* (Fourth Edition) WHO Library Cataloguing- in-publication data, NLM classification. Washington, 541pp

Yakubu, S. (2008): The impact of industrial effluent on the adjacent environment in Bompai Industrial Eastate, Kano Unpub. B.sc Dissertation. Dept. of Geography, BUK Kano.

Zuidema, F. C. (1974): *Hydrological effect of Urbanization in the Netherlands*. Hydrological effects of Urbanization studies and reports in Hydrology 18 praise. The UESCO Press.