



UNIVERSITI PUTRA MALAYSIA

***PREDICTION OF NITRATE –NITROGEN LEACHING IN PADDY SOIL
USING MULTIVARIATE ANALYSIS AND ARTIFICIAL NEURAL
NETWORK***

HAZILIA BINTI HUSSAIN

FPAS 2012 15

**PREDICTION OF NITRATE-NITROGEN
LEACHING IN PADDY SOIL USING
MULTIVARIATE ANALYSIS AND ARTIFICIAL
NEURAL NETWORK**



HAZILIA BINTI HUSSAIN

**DOCTOR OF PHILOSOPHY
UNIVERSITI PUTRA MALAYSIA**

2012

**PREDICTION OF NITRATE –NITROGEN LEACHING IN PADDY SOIL
USING MULTIVARIATE ANALYSIS AND ARTIFICIAL NEURAL
NETWORK**

By

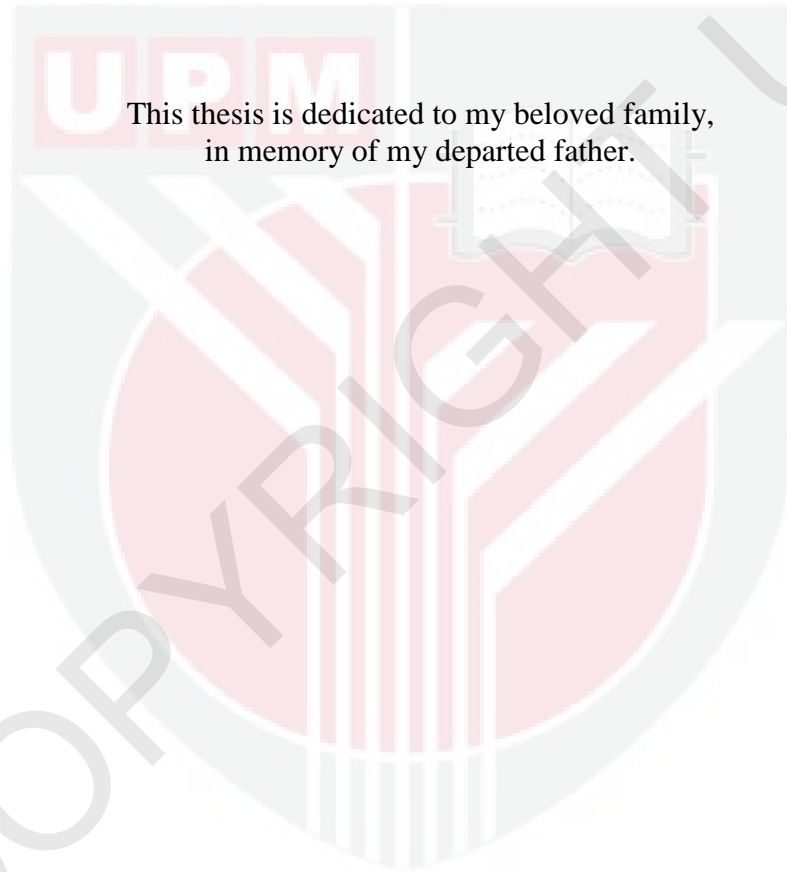
HAZILIA BINTI HUSSAIN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

April 2012

DEDICATION

This thesis is dedicated to my beloved family,
in memory of my departed father.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment
of the requirement for the degree of Doctor of Philosophy

**PREDICTION OF NITRATE –NITROGEN LEACHING IN PADDY SOIL
USING MULTIVARIATE ANALYSIS AND ARTIFICIAL NEURAL
NETWORK**

By

HAZILIA BINTI HUSSAIN

April 2012

Chairman: Associate Professor Mohd Kamil Yusoff, PhD

Faculty: Environmental Studies

Nitrate-nitrogen leaching from agricultural areas is a major cause for groundwater pollution. Polluted groundwater with high levels of nitrate is hazardous and causes adverse health effects. This research aims to study nitrate–nitrogen leaching into groundwater in paddy soils at Ladang Merdeka Ismail Mulong in Kelantan, Malaysia. The assessment of soil physical properties and groundwater quality, effect of fertilizer on the groundwater nitrate-nitrogen concentrations, identification of contributory factors and prediction of nitrate-nitrogen leaching using computer modeling were the specific objectives of this study.

A total of twelve observation wells and sixteen privately-owned wells were selected for groundwater quality monitoring. Their physical properties were measured by ASTM method while the concentrations of nitrate-nitrogen, phosphate and potassium were analyzed according to US-EPA 300.0, 365.2 and 200.2 procedures, respectively. Groundwater nitrate-nitrogen concentration ranged from 0.0 to 3.85 mg NO₃⁻-N/l in the observation wells and 0.0 to 5.08 mg NO₃⁻-N/l in the private-owned wells. These values fall below the permissible limit of 10 mg/l nitrate-nitrogen. However, the increasing trends of nitrate-nitrogen concentrations in the wells are of concern because it might accumulate over time and pollute the groundwater.

The phosphate concentrations in 54.2% of observation wells and 36.7% of private-owned wells exceeded the permissible standard of 0.2 mg/l. The high values of phosphate could create problems related to the taste and odor of the water. The soil texture was classified as clay based on the United States Department of Agriculture (USDA) soil textural classification system. The results of soil bulk density (1.38 g/cm³), porosity (38.8%) and soil penetration resistance (1.48 MPascal) confirmed the existence of a hard pan within the soil profile; (1) topsoil (0-30cm), (2) hard pan (30-60 cm) and (3) subsoil (below 60 cm).

Nitrate leaching at different soil depths (20, 30 and 40 cm) was monitored using soil suction samplers for two consecutive seasons. The concentrations varied from 1.10-11.70 mg NO₃⁻-N /l and 1.20-3.78 mg NO₃⁻-N/l in the first and second season, respectively. The results showed that nitrate-nitrogen concentration in the soil increased with soil depth and higher fertilizer application indicating that fertilizer

application influences the leaching process which leads to the accumulation of nitrate-nitrogen in the soil. The total nitrogen loss was 0.93% to 1.30% of the applied nitrogen with the highest leaching rate at the 40 cm soil layer ($0.35 \text{ kg NO}_3^- \text{ N/ha/d}$) indicating soil contamination and causes nitrate build-up in the groundwater above permissible limit, thus rendering it unsuitable for human consumption.

The complex data matrix (128 x 16) of nitrate-nitrogen parameters was subjected to multivariate analysis mainly principal component analysis (PCA) and discriminant analysis (DA). PCA extracted four principal components from this data set which explained 86.4% of the total variance. Analysis using Alyuda Forecaster software confirmed that the most important contributors were soil physical properties ($R^2 = 0.98$). Discriminant analysis was used to evaluate the temporal variation in soil nitrate-nitrogen on leaching process. Discriminant analysis gave four parameters (hydraulic head, evapotranspiration, rainfall and temperature) contributing more than 98% correct assignments in temporal analysis. DA allowed reduction in dimensionality of the large data set which defines the four operating parameters most efficient and economical to be monitored for temporal variations.

Four different data sets were used to develop predictive nitrate-nitrogen models in an Artificial Neural Network (ANN) environment. The results showed good agreement between predicted and observed nitrate-nitrogen leaching rate for TD-ANN model with coefficient correlations of $R = 0.98$ in the testing step. Based on the principal component analysis scores, ANN generated two models, PCS-ANN1 and PCS-ANN2, which gave good predictions with $R = 0.97$ and 0.94 in their respective testing steps. An inspection of the results showed that ANN gave reliable predictive

models with acceptable accuracies. The results of this study indicate that ANN can be reliably used as a tool to predict nitrate-nitrogen leaching rates in paddy soils based on the selected sixteen parameters.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**RAMALAN PENGURASAN NITRAT-NITROGEN DI DALAM TANAH
PADI MENGGUNAKAN ANALISIS MULTIVARIAT DAN RANGKAIAN
NEURAL TIRUAN**

Oleh

HAZILIA BINTI HUSSAIN

April 2012

Pengerusi: Profesor Madya Mohd Kamil Yusoff, PhD

Fakulti: Pengajian Alam Sekitar

Pengurusan nitrat-nitrogen dari kawasan pertanian adalah punca utama bagi pencemaran air bawah tanah. Air bawah tanah yang tercemar dengan tahap nitrat yang tinggi adalah berbahaya dan menyebabkan kesan mudarat ke atas kesihatan. Kajian ini bertujuan untuk mengkaji pengurusan nitrat-nitrogen ke dalam air bawah tanah di tanah padi di Ladang Merdeka Ismail Mulong di Kelantan, Malaysia. Penilaian sifat fizikal tanah dan kualiti air bawah tanah, kesan baja ke atas kepekatan nitrat-nitrogen air bawah tanah, mengenalpasti faktor-faktor penyumbang dan ramalan pengurusan nitrat-nitrogen menggunakan pemodelan komputer adalah objektif khusus kajian ini.

Sebanyak dua belas telaga pemerhatian dan enam belas telaga milik persendirian telah dipilih untuk pemantauan kualiti air bawah tanah. Sifat fizikal air bawah tanah telah diukur dengan kaedah ASTM manakala kepekatan nitrat-nitrogen, fosfat dan kalium dianalisis mengikut prosedur US-EPA 300.0, 365.2 dan 200.2 masing-masing. Kepekatan nitrat-nitrogen dalam air bawah tanah adalah 0.0-3.85 mg NO_3^- -N / l untuk telaga pemerhatian dan 0.0 hingga 5.08 mg NO_3^- -N / l dalam telaga milik persendirian. Nilai ini rendah daripada had yang dibenarkan sebanyak 10 mg / l nitrat-nitrogen. Walau bagaimanapun, trend peningkatan kepekatan nitrat-nitrogen dalam telaga membimbangkan kerana ia mungkin terkumpul dari masa ke semasa dan mencemarkan air bawah tanah. Keputusan bagi kepekatan fosfat menunjukkan bahawa 54.2% daripada telaga pemerhatian dan 36.7% daripada telaga persendirian melebihi standard dibenarkan iaitu 0.2 mg / l. Nilai-nilai fosfat yang tinggi boleh menimbulkan masalah yang berkaitan dengan rasa dan bau air tersebut. Tekstur tanah telah dikelaskan sebagai tanah liat yang berdasarkan sistem klasifikasi tekstur tanah Jabatan Pertanian Amerika Syarikat (USDA). Keputusan ketumpatan pukal tanah (1.38 g/cm^3), keliangan (38.8%) dan rintangan penembusan tanah (1.48 MPascal) mengesahkan kewujudan lapisan kemasu dalam profil tanah; (1) tanah atas (0-30cm), (2) lapisan kemasu (30-60 cm) dan (3) subtanah (di bawah 60 cm).

Pengurusan nitrat pada kedalaman tanah yang berlainan (20, 30 dan 40 sm) telah dipantau dengan menggunakan alat penyedut air tanah ("soil suction samplers") untuk dua musim berturut-turut. Variasi kepekatan adalah dari 1.10-11.70 mg NO_3^- -N / l dan 1.20-3.78 mg NO_3^- -N/l dalam musim pertama dan kedua, masing-masing.

Hasil kajian

menunjukkan bahwa kepekatan nitrat-nitrogen di dalam tanah meningkat dengan kedalaman tanah dan penggunaan baja yang lebih tinggi membuktikan bahwa penggunaan baja mempengaruhi proses pengurasan yang membawa kepada pengumpulan nitrat-nitrogen di dalam tanah. Jumlah keseluruhan kehilangan nitrogen adalah 0.93% hingga 1.30% daripada baja nitrogen yang digunakan dengan kadar resapan yang tinggi di lapisan tanah 40 sm ($0.35 \text{ kg NO}_3^- \text{-N/ha/h}$) menunjukkan pencemaran tanah dan menyebabkan pengumpulannya dalam air bawah tanah melebihi had yang dibenarkan, dan ini menjadikannya tidak sesuai untuk kegunaan manusia.

Matriks data parameter nitrat-nitrogen yang kompleks (128×16) telah dianalisa dengan multivariat terutamanya analisis komponen utama (PCA) dan analisis diskriminan (DA). PCA mengekstrak empat komponen utama daripada set data ini yang menjelaskan 86.4% daripada jumlah varians. Analisis menggunakan perisian Peramal Alyuda telah mengesahkan penyumbang yang paling penting adalah sifat fizikal tanah ($R^2 = 0.98$). Analisis diskriminan digunakan untuk menilai variasi masa proses pengurasan nitrat-nitrogen dalam tanah. Analisis diskriminan memberikan empat parameter (tekanan hidraulik, evapotranspirasi, hujan dan suhu) menyumbang lebih daripada 98% ramalan yang betul dalam analisis masa. DA membenarkan pengurangan dalam dimensi set data yang besar yang mentakrifkan empat parameter operasi yang paling cekap dan ekonomi untuk dipantau bagi variasi masa.

Empat set data yang berbeza telah digunakan untuk membangunkan model ramalan nitrat-nitrogen dalam persekitaran Rangkaian Neural Tiruan (ANN). Keputusan

menunjukkan korelasi kadar resapan nitrat -nitrogen yang baik antara diramalkan dan diperhatikan untuk model TD-ANN dengan korelasi pekali $R = 0.98$ dalam peringkat ujian. Berdasarkan analisis skor komponen utama, ANN menjana dua model, PCS-ANN1 dan PCS-ANN2, yang memberikan ramalan yang baik dengan $R = 0.97$ dan 0.94 dalam peringkat ujian masing-masing. Pemeriksaan keputusan menunjukkan bahawa ANN memberikan model ramalan yang dipercayai dengan ketepatan yang boleh diterima. Keputusan kajian ini menunjukkan bahawa ANN sesuai digunakan sebagai alat untuk meramal kadar pengurusan nitrat-nitrogen dalam tanah padi berdasarkan enam belas parameter yang dipilih.

ACKNOWLEDGEMENTS

The completion of this research could not have been possible without the support and assistance from the following people. First and foremost I would like to express my deepest gratitude to my project supervisor, Assoc. Prof. Dr. Mohd Kamil Yusoff for his patience, concern and guidance throughout this study. I am grateful to my co-supervisors, Assoc. Prof. Dr. Mohamed Firuz Ramli and Assoc. Prof. Dr. Puziah Abd Latiff for their valuable advice, guidance and their patience in reading my thesis. My heartiest thanks are for Dr. Hafizan Juahir who has guided me in understanding multivariate analysis and Cik Munira for helping me with some data analysis.

Sincere thanks and appreciation goes to En Abdul Rashid, En Zamani, En Shahrudin and all staff of Professional Environmental Services (PES), Universiti Putra Malaysia for their assistance in the laboratory and field work. My upmost thanks are also extended to En. Mohd Azwan Mohd Zawawi from Department of Agriculture and Biological Engineering, UPM, who was most helpful in the field work and he was pivotal in my understanding of soil physics. I am also appreciative of the tireless assistance from the technicians at his department during the field work. I am really grateful for the time each of you spent in helping me to achieve this goal.

Field research for this study was conducted at Ladang Merdeka Ismail Mulong under the Kemubu Agricultural Development Agency (KADA), Kelantan. I wish to thank

this organization for their cooperation and contributions during the course of this study.

Most importantly, I wish to thank Universiti Technology Mara and Public Services Department of Malaysia for financing my studies at UPM. Lastly, special thanks to my husband, Abd Rashid Mohd Nor, children and friends for their support and patience throughout this challenging period of my life.



I certify that a Thesis Examination Committee has met on 17 April 2012 to conduct the final examination of Hazilia binti Hussain on her thesis entitled “Prediction of Nitrate-Nitrogen Leaching in Paddy Soil Using Multivariate Analysis and Artificial Neural Network” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Degree Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Ahmad Makmom bin Abdullah, PhD

Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

Mohd Razi bin Ismail, PhD

Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Nik Muhamad bin Nik Majid, PhD

Faculty of Forestry
Universiti Putra Malaysia
(Internal Examiner)

Kyoung-Woong Kim, PhD

Professor
Gwangju Institute of Science and Technology
Korea
(External Examiner)

SEOW HENG FONG, Ph

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 28 June 2012

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mohd Kamil Yusoff, PhD

Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

Mohamed Firuz Ramli, PhD

Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Member)

Puziah Abd. Latiff, PhD

Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Member)

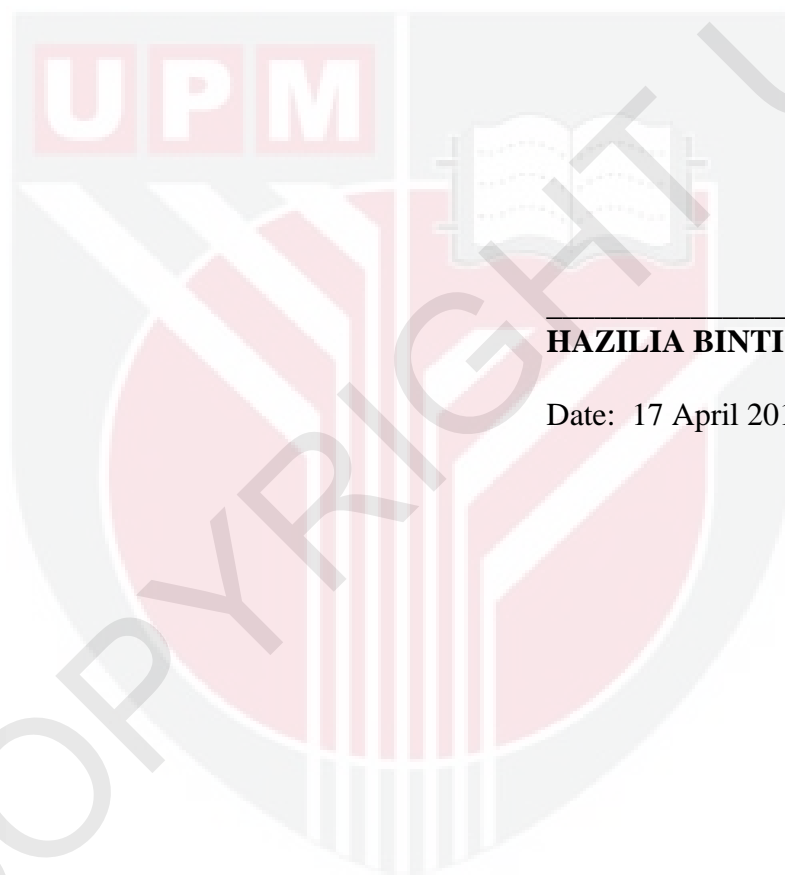
BUJANG BIN KIM HUAT, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or any other institution.



HAZILIA BINTI HUSSAIN

Date: 17 April 2012.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ABSTRAK	vii
ACKNOWLEDGEMENTS	xi
APPROVAL	xiii
DECLARATION	xv
LIST OF TABLES	xix
LIST OF FIGURES	xxii
LIST OF ABBREVIATIONS	xxvi
CHAPTER	
1 INTRODUCTION	
1.1 Awareness of Nitrate Pollution in Groundwater	1
1.2 Problems and Importance of the Study	
1.2.1 Groundwater Contamination in Malaysia	2
1.2.2 Rice Cultivation in Malaysia	4
1.2.3 Nitrate Losses via Leaching	5
1.2.4 Health Risks of Human Consumption of Nitrates	7
1.3 Aims of the Study	8
1.4 Scope of the Study	10
1.5 Significance of Study	11
2 BACKGROUND AND LITERATURE REVIEW	
2.1 Physiography of Study Site	12
2.2 Geology and Hydrogeology of Study Area	13
2.3 Kemubu Agricultural Development Authority (KADA)	15
2.4 Groundwater and Groundwater Quality Monitoring	17
2.5 Groundwater Utilization	17
2.6 Groundwater Pollution	18
2.7 Nitrogen Transformation in Rice Soils	21
2.8 Importance of Rice and Characteristics of Paddy Soils	22
2.9 Solute and Water Movement in Soils	24
2.10 Nitrate Leaching in Soils	25
2.11 Guidelines for Inorganic Fertilizer Practices in Malaysia and Comparisons with other Countries	28
2.12 Sampling Methods for Nitrate Leaching	32
2.13 Models for Nitrate Leaching	33
2.14 Determination of Nitrate-Nitrogen Leaching	35
2.15 Soil Penetration Resistance and Hydraulic Conductivity	37
2.16 Soil Water Pressure	39
2.17 Principal Component Analysis (PCA)	41
2.18 Theoretical Concepts and Structure of Artificial Neural Network (ANN)	43
2.19 Discriminant Analysis (DA)	45
2.20 Health Impact of Nitrate	46
3 METHODOLOGY	
3.1 Description of Study Area	49

3.2	Determination of Physical and Chemical Characteristics of Groundwater in Observation and Private Wells	
3.2.1	Installation of Observation Wells	52
3.2.2	Groundwater Sampling	53
3.3	Determination of Distribution Pattern, Concentration and Variation of Nitrate-Nitrogen Levels in the Soils at Different Depths	56
3.3.1	Crop Management Practice	56
3.3.2	Installation of Lysimeter in Experimental Plot	57
3.4	Methods of Field Measurement	
3.4.1	Soil Solution Sampling	58
3.4.2	Determination of Pressure Head	61
3.4.3	Determination of Soil Penetration Resistance	62
3.4.4	Soil Sampling	62
3.5	Laboratory Analysis	63
3.5.1	Determination of Nitrate-Nitrogen Concentration in Soil Solution	63
3.5.2	Determination of Soil Physical Properties	63
3.6	Calculation of Water Flux	65
3.7	Quantification of Nitrate-Nitrogen Leaching	65
3.8	Secondary Data- Meteorological and Hydraulic Conductivity	66
3.9	Data Analysis and Modeling	66
3.10	Methodology of Parameters Used in Multivariate Analysis	68
3.11	Principal Component Analysis (PCA)	70
3.12	Predictive Models Using Artificial Neural Network (ANN)	72
3.12.1	Raw Data ANN (RD-ANN)	73
3.12.2	Treated Data ANN (TD-ANN)	73
3.12.3	Principal Component Scores (PCS-ANN)	74
3.12.4	Principal Component Scores (PCS-ANN)	75
3.13	Models Performances Indexes	76
3.14	Data Analysis for Temporal Variations	77
4	RESULTS AND DISCUSSION	
4.1	Introduction	79
4.2	Soil Physical Properties of Study Area	80
4.2.1	Particle Size Distribution and Soil Textural Classification	80
4.2.2	Bulk Density, Dry Bulk Density, Particle Density and Porosity of the Soil	81
4.2.3	Soil Penetration Resistance (SPR) and Water Content	82
4.3	Results of Evapotranspiration, Rainfall and Temperature	84
4.4	Results of Variation of Pressure Head and Hydraulic Gradient	85
4.5	Results of Groundwater Quality	86
4.5.1	Descriptive Tests for Groundwater Quality	86
4.5.2	Concentration of NPK in Different Villages	92
4.5.3	Groundwater Level Variation of Study Area	93
4.6	Results of Variation of Nitrate-Nitrogen Concentration in Soil Solution at Different Depths	95

4.7	Results of Average Nitrate-Nitrogen Leaching Rate	101
4.7.1	Amount of Nitrate-Nitrogen Leached	101
4.7.2	Relationship between Nitrate-Nitrogen Leaching and Rainfall	107
4.8	Results of Principal Component Analysis (PCA)- Source Apportionment	109
4.9	Forecast of leaching rate using Alyuda Forecaster XL software	114
4.10	Temporal variations	116
4.11	Nitrate leaching predictive models using Artificial Neural Network (ANN)	123
4.12	Results of models performances indexes	134
5	CONCLUSION	136
6	RECOMMENDATIONS FOR FUTURE RESEARCH	145
	REFERENCES	149
	APPENDICES	167
	BIODATA OF STUDENT	211
	LIST OF PUBLICATIONS	213