

**TRANSPORT OF NITRATE AND ITS FATE IN AN UNCONFINED  
SANDY AQUIFER OF GAREH-BYGON PLAIN, ISLAMIC  
REPUBLIC OF IRAN**

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**By**

**MEHRDAD MOHAMMADNIA**

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

**February 2007**

## **DEDICATION**

**Dedicated to late Imam Khomeyni, the enlightener and messiah of Iranian  
people,  
and to my dear family  
in memory of my departed father, mother and brother (Hedayat)**

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

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**February 2007**

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**Faculty: Agriculture**

In response to the growing awareness of groundwater and surface water degradation, there has been increased concern about  $\text{NO}_3^-$  mobility and retention in soils. Artificial recharge of groundwater (ARG) through floodwater spreading systems (FWSS) is conducted in the Gareh-Bygon Plain (GBP), south east of Iran, to facilitate both drinking and irrigating water for desert dwellers. However, floodwater used for ARG, contains  $60.30 \text{ mg L}^{-1} \text{ NO}_3^-$  on average and may contaminate groundwater. The main objective of this study was to identify the most suitable place for extracting safe drinking water supply in the GBP. Identifying natural sources and main flow pathways of  $\text{NO}_3^-$ , impacts of different landuse on the groundwater  $\text{NO}_3^-$  concentration, removal processes of  $\text{NO}_3^-$ , and predicting  $\text{NO}_3^-$  transport using suitable computer model, were specific objectives of this study.

In the first study, 30 random geologic materials from the BZB were sampled and analyzed for  $\text{NO}_3^-$  concentration. This was carried out for atmospheric deposition

during 27 rainfall events. Moreover, surficial floodwater and incoming groundwater as flow pathways into the aquifer, were monitored monthly and analyzed for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , dissolved  $\text{O}_2$  (DO), total organic carbon (TOC),  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}$ ,  $\text{Mn}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{CO}_3^{-2}$ ,  $\text{HCO}_3^-$ , alkalinity, EC and pH. Results showed  $\text{NO}_3^-$  concentration in the geologic materials ranged from 0.94 to 123.31  $\text{mg kg}^{-1}$ , however, that of the atmospheric deposition ranged from 0.88 to 19.12  $\text{mg L}^{-1}$ . The concentrations of  $\text{NO}_3^-$  in the incoming groundwater ranged from 1.50 to 39.94  $\text{mg L}^{-1}$ . Predominance of the oxidizing condition supports  $\text{NO}_3^-$  stability in the flow pathways and in the aquifer as well. As a consequence, geologic materials and atmospheric deposition were not responsible for the serious  $\text{NO}_3^-$  concentrations in the BZ groundwater.

The impact of different landuse on the groundwater  $\text{NO}_3^-$  concentration was investigated during the 12 months monitoring for the 2<sup>nd</sup> study (from 2003 to April 2004). Samples were analyzed for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , DO, TOC,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}$ ,  $\text{Mn}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{CO}_3^{-2}$ ,  $\text{HCO}_3^-$ , alkalinity, EC and pH. Groundwater  $\text{NO}_3^-$  concentration ranged from 0.02  $\text{mg L}^{-1}$  in the recharge area to 94.45  $\text{mg L}^{-1}$  in the farming area which was higher than the permitted level of that ion in drinking water by United States Environmental Protection Agency (USEPA). Both farming areas, upstream and downstream the FWSS, increased  $\text{NO}_3^-$  concentration in the groundwater. However, recharge flow decreased groundwater  $\text{NO}_3^-$  through FWSS. Consequently, recharge area was found to be the most suitable and supply safe drinking water to inhabitants.

In the 3<sup>rd</sup> study, the possible NO<sub>3</sub><sup>-</sup> removal processes in the GBP was investigated through; i) absorption, ii) adsorption, and iii) dilution. Planted and non-planted packed leaching columns in saturated and semi-saturated conditions were examined in the laboratory and in the open field, respectively. Results for semi-saturated condition showed the average NO<sub>3</sub><sup>-</sup> concentration in the planted leachate fractions (4.15 mg/L) was 6.54 times less than that of the control (27.15 mg/L). Breakthrough curve (BTC) obtained for saturated columns was asymmetric. Small average retardation factors,  $R = 2.38$  and  $R \approx 0.00$ , for planted and non-planted columns, respectively, suggested non-significant NO<sub>3</sub><sup>-</sup> absorption by seedlings in saturated condition. This implies the potential of the Eucalyptus forested area to take NO<sub>3</sub><sup>-</sup> up from the recharge water flow in the real FWSS.

Batch adsorption isotherms and envelope tests were carried out for soil, sediment, and pure palygorskite as a vertical translocated clay species into the forested Eucalyptus rhizosphere. Results of all adsorption isotherms were best fitted to the Langmuir equation. Maximum NO<sub>3</sub><sup>-</sup> adsorption occurred at  $\text{pH} < (\text{PZC} = 6.53)$  of the soil. Dilution was documented as the most effective NO<sub>3</sub><sup>-</sup> removal process in the BZ aquifer using the average NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> concentrations.

The HYDRUS-1D was found to be a useful software for predicting vertical nitrate transport through saturated soil column. Nitrate BTC obtained from leaching columns and simulated data were compatible in general. Nitrate distribution pattern throughout the BZ aquifer was also simulated successfully using a MODFLOW\_PMPATH computer code.

As the main result of this study, it was found that the most suitable drinking water for the rural people in the BZB is the water extracted from wells located in the forested recharge area. However, the most degraded water was found in the vicinity of the farming areas.

**Keywords:** Nitrate pollution, Drinking water, Denitrification, Artificial recharge, Floodwater spreading system, HYDRUS model, MODFLOW model.

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

**PENGANGKUTAN NITRAT DALAM AKUIFER BERPASIR TIDAK  
TERBENDUNG, DATARUN GAREH-BYGON, I. R. IRAN**

Oleh

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**Februari 2007**

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Memandangkan kesedaran yang semakin meningkat terhadap degradasi air bawah tanah dan air permukaan, tumpuan telah diberikan terhadap pergerakan dan pengekalan  $\text{NO}_3^-$  dalam tanah. Recas buatan air bawah tanah (ARG) melalui sistem penyebaran banjir (FWSS) dijalankan di dataran Gareh-Bygon (GBP), di tenggara Iran, untuk memudahkan pengairan dan penyaliran air minuman untuk penduduk di padang pasir. Namun, air banjir yang digunakan untuk ARG mengandungi kepekatan purata sebanyak  $60.30 \text{ mg L}^{-1}$  dan boleh mengakibatkan kontaminasi berlaku pada air bawah tanah. Objektif utama kajian ini ialah untuk mengenalpasti kawasan yang paling sesuai untuk mengesktrak bekalan air minuman yang selamat di GBP. Pengenalpastian sumber  $\text{NO}_3^-$  semulajadi dan laluan aliran utama  $\text{NO}_3^-$ , kesan gunat tanah yang berbeza ke atas kepekatan  $\text{NO}_3^-$  dalam air bawah tanah, proses penyahan  $\text{NO}_3^-$ , dan menganggarkan pengangkutan  $\text{NO}_3^-$  menggunakan model berkomputer yang bersesuaian, merupakan objektif-objektif spesifik untuk kajian ini.

Dalam kajian pertama, 30 bahan geologi dari BZB disampel secara rawak dan dianalisa untuk  $\text{NO}_3^-$ . Ini dilakukan untuk mendapan dari atmosfera sebagai salah satu dari sumber potensi  $\text{NO}_3^-$  semasa 27 episod hujan. Juga, air permukaan semasa banjir dan air bawah tanah sebagai laluan aliran masuk ke akuifer, dipantau tiap-tiap bulan dan dianalisis untuk  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{O}_2$  (DO) terlarut, jumlah karbon organik (TOC),  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}_t$ ,  $\text{Mn}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{CO}_3^{-2}$ ,  $\text{HCO}_3^-$ , kealkalian, kekonduksian elektrik (EC) dan pH. Keputusan menunjukkan bahawa julat kepekatan  $\text{NO}_3^-$  dalam bahan geologi adalah di antara 0.94 hingga 123.31  $\text{mg kg}^{-1}$ , bagaimanapun, mendapan dari atmosfera adalah dari 0.88 hingga 19.12  $\text{mg L}^{-1}$ . Julat kepekatan nitrat dalam air bawah tanah ialah di antara 1.50 hingga 39.94  $\text{mg L}^{-1}$ . Keadaan teroksida yang dominan mempengaruhi kestabilan nitrat dalam air aliran dan juga akuifer. Adalah didapati, bahan geologi dan mendapan atmosfera bukanlah sumber yang bertanggungjawab keatas kontaminasi nitrat yang serius dalam air bawah tanah BZ.

Kesan daripada guna-tanah yang berbeza ke atas kepekatan  $\text{NO}_3^-$  dalam air bawah tanah dipantau selama 12 bulan untuk kajian kedua. Sampel diuji untuk  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{O}_2$  terlarut, jumlah karbon organik (TOC),  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}_t$ ,  $\text{Mn}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{CO}_3^{-2}$ ,  $\text{HCO}_3^-$ , kealkalian, EC dan pH. Julat kepekatan nitrat dalam air bawah tanah ialah 0.02  $\text{mg L}^{-1}$  di kawasan recas sehingga 94.45 di kawasan pertanian, iaitu, takat yang lebih tinggi dari had maksimum untuk ion tersebut yang dibenarkan dalam air minuman oleh Agensi Perlindungan Alam Sekitar, U.S.A. Kedua-dua kawasan pertanian, satu di hulu dan satu lagi di hilir dari FWSS menunjukkan peningkatan kepekatan nitrat dalam air bawah tanah. Namun demikian, aliran recas mengurangkan kepekatan nitrat dalam air bawah tanah. Oleh itu, kawasan recas adalah merupakan

kawasan yang paling sesuai dan membekalkan air minuman yang selamat untuk penduduk.

Dalam kajian yang ketiga, proses penyahan  $\text{NO}_3^-$  yang mungkin berlaku di GBP ditentukan melalui; i) penyerapan  $\text{NO}_3^-$  oleh anak benih Eucalyptus dalam keadaan tepu dan separa tepu, ii) penjerapan  $\text{NO}_3^-$  oleh tanah dan sampel mendapan baru, dan iii) pencairan oleh  $\text{NO}_3^-$  oleh ARG. Turus luluhlarutan dengan dan tanpa tanaman pada keadaann tepu atau separa tepu air dikaji di makmal dan di lapangan. Keputusan untuk keadaan separa tepu menunjukkan purata kepekatan nitrat ( $4.15 \text{ mg L}^{-1}$ ) pada turus luluhlarutan dengan tanaman adalah 6.54 kali lebih rendah daripada rawatan kawalan ( $27.15 \text{ mg L}^{-1}$ ). Lekuk kemunculan (BTC) yang diperolehi untuk keadaan tepuair tak simetri. Bagaimanapun, faktor retardasi purata yang kecil  $R = 2.38$ , dan  $R \approx 0.00$  telah diperolehi dari rawatan dengan tanaman dan tanpa tanaman, mengikut susunan, yang mencadangkan penyerapan  $\text{NO}_3^-$  secara tidak signifikan oleh anak benih dalam keadaan tepu. Ini memberi implikasi potensi kawasan hutan Eucalyptus untuk menyerap nitrat dari kawasan aliran air recas di FWSS yang sebenarnya.

Isoterma jerapan sesekumpul dan ujikaji “envelope” dijalankan ke atas tanah, sampel mendapan dan palygorskite tulen yang merupakan lempung yang mengalami proses translokasi menegak dan pengumpulan pada rizosfera hutan Eucalyptus. Hasil daripada semua isoterma jerapan mempunyai suaian terbaik dengan persamaan Langmuir. Perbezaan dalam luas permukaan spesifik  $\text{CaCO}_3$  berfungsi mengawal jerapan  $\text{NO}_3^-$  oleh  $\text{CaCO}_3$ . Jerapan maksimum  $\text{NO}_3^-$  berlaku pada pH lebih rendah dari titik cas sifar (PZC) = 6.53 seperti ukuran  $\text{pH}_0$  pada sampel tanah. Pencairan

nitrat telah didokumentasikan sebagai proses pengurangan  $\text{NO}_3^-$  yang paling efektif dalam air bawah tanah BZ dengan menggunakan konsentrasi purata  $\text{NO}_3^-/\text{Cl}^-$  sepanjang kajian dijalankan.

HYDRUS-1D merupakan perisian yang digunakan untuk menganggarkan pengangkutan nitrat secara menegak melalui turus tanah tepu air. Keluk kemunculan nitrat yang diperolehi dari turus luluhlarutan dan data simulasi adalah berpadanan secara amnya. Corak taburan nitrat sepanjang laluan air bawah tanah BZ, berjaya dianggarkan menggunakan kod berkomputer MODFLOW\_PMPATH.

Hasil utama daripada kajian ini menunjukkan bahawa air minuman yang paling sesuai untuk penduduk pedalaman di BZB patut diekstrak dari perigi-perigi yang terletak di kawasan recas buatan. Walaubagaimanapun, air paling terdegradasi dijumpai di kawasan yang hampir dengan kawasan pertanian.

**Kata kunci:** Pencemaran nitrat, Air minuman, Denitrifikasi, Recas buatan, Sistem sebaran banjir, Model HYDRUS, Model MODFLOW

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I certify that an Examination Committee has met on 15 February 2007 to conduct the final examination of Mehrdad Mohammadnia on his Doctor of Philosophy thesis entitled “Transport of Nitrate and its Fate in an Unconfined Sandy Aquifer of Gareh-Bygon Plain, Islamic Republic of Iran” in accordance with Universiti Pertanian Malaysia Act 1980 and Universiti Putra Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 12 April 2007

## **DECLARATION**

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

**MEHRDAD MOHAMMADNIA**

Date: 15 March 2007

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## LIST OF ABBREVIATIONS

Ads <sub>.max</sub>	Maximum Adsorption
AEC	Anion Exchange Capacity
AJF	Agha-Jari Formation
AMP	Aquifer Management Project
ARG	Artificial Recharge of Groundwater
BZB	Bisheh- Zard Basin
BZ1	Bisheh-Zard One
BZ4	Bisheh-Zard Four
CCE	Calcium Carbonate Equivalent
CEC	Cation Exchange Capacity
DI	De Ionized
DO	Dissolved Oxygen
EC	Electrical Conductivity
FFZ	Forested Filter Zone
FWSS	Flood Water Spreading System
GBP	Gareh Bygon Plain
GW	Groundwater
HTAS	High Affinity Transport System
ICP	Inductively Coupled Plasma
IS	Ionic Strength
LATS	Low Affinity Transport System
OM	Organic Matter
PZC	Point of Zero Charge

RA2	Rahim Abad Two
SB	Sedimentation Basin
SSA	Specific Surface Area
TA	Total Alkalinity
TC	Total Carbon
TDL	Theoretical Dilution Line
TEM	Transmission Electron Micrograph
TH	Total Hardness
TIC	Total Inorganic Carbon
TN	Total Nitrogen
TOC	Total Organic Carbon
PV	Pore Volume
PVC	Poly Vinyl Chloride
USEPA	United State Environmental Protection Agency
WHO	World Health Organization
XRD	X-ray Diffractogram