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

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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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Chairman: Associate Professor Che Fauziah Ishak, PhD

Faculty: Agriculture

In response to the growing awareness of groundwater and surface water degradation, there has been increased concern about 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 mg L^{-1} 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 NO_3^-, impacts of different landuse on the groundwater NO_3^- concentration, removal processes of NO_3^-, and predicting 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 NO_3^- concentration. This was carried out for atmospheric deposition

during 27 rainfall events. Moreover, surfacial floodwater and incoming groundwater as flow pathways into the aquifer, were monitored monthly and analyzed for NO_3^-, NH_4^+, dissolved O_2 (DO), total organic carbon (TOC), Na^+, K^+, Ca^{+2}, Mg^{+2}, Fe_t, Mn^{+2}, Cl^-, SO_4^{-2}, CO_3^{-2}, HCO_3^-, alkalinity, EC and pH. Results showed NO_3^- concentration in the geologic materials ranged from 0.94 to 123.31 mg kg^{-1}, however, that of the atmospheric deposition ranged from 0.88 to 19.12 mg L^{-1}. The concentrations of NO_3^- in the incoming groundwater ranged from 1.50 to 39.94 mg L^{-1}. Predominance of the oxidizing condition supports 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 NO_3^- concentrations in the BZ groundwater.

The impact of different landuse on the groundwater NO_3^- concentration was investigated during the 12 months monitoring for the 2nd study (from 2003 to April 2004). Samples were analyzed for NO_3^-, NH_4^+, DO , TOC, Na^+, K^+, Ca^{+2}, Mg^{+2}, Fe_t, Mn^{+2}, Cl^-, SO_4^{-2}, CO_3^{-2}, HCO_3^-, alkalinity, EC and pH. Groundwater NO_3^- concentration ranged from 0.02 mg L^{-1} in the recharge area to 94.45 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 NO_3^- concentration in the groundwater. However, recharge flow decreased groundwater NO_3^- through FWSS. Consequently, recharge area was found to be the most suitable and supply safe drinking water to inhabitants.

In the 3rd study, the possible NO_3^- 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_3^- 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_3^- absorption by seedlings in saturated condition. This implies the potential of the Eucalyptus forested area to take NO_3^- 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_3^- adsorption occurred at pH < (PZC = 6.53) of the soil. Dilution was documented as the most effective NO_3^- removal process in the BZ aquifer using the average NO_3^-/ Cl^- 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

MEHRDAD MOHAMMADNIA

Februari 2007

Pengerusi: **Professor Madya Che Fauziah Ishak, PhD**

Fakulti: **Pertanian**

Memandangkan kesedaran yang semakin meningkat terhadap degradasi air bawah tanah dan air permukaan, tumpuan telah diberikan terhadap pergerakan dan pengekalan 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 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 NO_3^- semulajadi dan laluan aliran utama NO_3^-, kesan guna-tanah yang berbeza ke atas kepekatan NO_3^- dalam air bawah tanah, proses penyahan NO_3^-, dan menganggarkan pengangkutan 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 NO_3^-. Ini dilakukan untuk mendapan dari atmosfera sebagai salah satu dari sumber potensi 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 NO_3^-, NH_4^+, O_2 (DO) terlarut, jumlah karbon organik (TOC), Na^+, K^+, Ca^{+2}, Mg^{+2}, Fe_t, Mn^{+2}, Cl^-, SO_4^{-2}, CO_3^{-2}, HCO_3^-, kealkalian, kekonduksian elektrik (EC) dan pH. Keputusan menunjukkan bahawa julat kepekatan NO_3^- dalam bahan geologi adalah di antara 0.94 hingga 123.31 mg kg^{-1}, bagaimanapun, mendapan dari atmosfera adalah dari 0.88 hingga 19.12 mg L^{-1} . Julat kepekatan nitrat dalam air bawah tanah ialah di antara 1.50 hingga 39.94 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 NO_3^- dalam air bawah tanah dipantau selama 12 bulan untuk kajian kedua. Sampel diuji untuk NO_3^-, NH_4^+, O_2 terlarut, jumlah karbon organik (TOC), Na^+, K^+, Ca^{+2}, Mg^{+2}, Fe_t, Mn^{+2}, Cl^-, SO_4^{-2}, CO_3^{-2}, HCO_3^-, kealkalian, EC dan pH. Julat kepekatan nitrat dalam air bawah tanah ialah 0.02 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 NO_3^- yang mungkin berlaku di GBP ditentukan melalui; i) penyerapan NO_3^- oleh anak benih Eucalyptus dalam keadaan tepu dan separa tepu, ii) penjerapan NO_3^- oleh tanah dan sampel mendapan baru, dan iii) pencairan oleh 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 mg L^{-1}) pada turus luluhlarutan dengan tanaman adalah 6.54 kali lebih rendah daripada rawatan kawalan (27.15 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 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 $CaCO_3$ berfungsi mengawal jerapan NO_3^- oleh $CaCO_3$. Jerapan maksimum NO_3^- berlaku pada pH lebih rendah dari titik cas sifar (PZC) = 6.53 seperti ukuran pH_o pada sampel tanah. Pencairan

nitrat telah didokumentasikan sebagai proses pengurangan NO_3^- yang paling efektif dalam air bawah tanah BZ dengan menggunakan konsentrasi purata NO_3^-/ 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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This thesis 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 are as follows:

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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.

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MEHRDAD MOHAMMADNIA

Date: 15 March 2007

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LIST OF ABBREVIATIONS

$Ads._{max}$	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