INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6” x 9” black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
IMPACT OF ARTIFICIAL GROUND WATER RECHARGE
AT TWO NEBRASKA SITES

by

Li Ma

A DISSERTATION

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy

Major: Agronomy

Under the Supervision of Professor Roy F. Spalding

Lincoln, Nebraska

May, 1996
Dissertation Title

Impact of Artificial Ground Water Recharge at Two Nebraska Sites

By

Li Ma

Supervisory Committee:

Approved

Dr. Roy F. Spalding
Typed Name

William L. Powers
Typed Name

Joseph M. Skopp
Typed Name

Dr. Vitaly Zlotnik
Typed Name

Date

4/12/96

4/12/96

4/12/96

4/12/96

Graduate College
University of Nebraska

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The dissertation research focuses on two ground water recharge projects. Herbicide behavior is interpreted in a watershed system with data collected from runoff, Recharge Lake and ground water at the York Ground Water Recharge Project. Maximum atrazine inputs to Recharge Lake occurred in spring runoff events and resulted in atrazine concentrations of 36 and 17 μg L$^{-1}$ in 1993 and 1994, respectively. Only about 0.28% and 0.19% of total applied atrazine was lost to runoff in 1993 and 1994. Atrazine concentrations in Recharge Lake decreased exponentially with degradation half-lives of 237 d in 1993 and 209 d in 1994. Adjusted DEA concentrations in Recharge Lake remained relatively constant, indicating little evidence for biotic degradation, and suggesting that abiotic degradation of atrazine to hydroxyatrazine was the most likely major degradative pathway in Recharge Lake. Maximum bromide concentrations obtained in the nearby aquifer represented only 27% of the initial concentration in Recharge Lake. The low detected concentrations might be due to the low infiltration rates and dilutions.

Effects of artificial recharge on ground water quality and quantity was studied at the Wood River Ground Water Recharge Project. A total of 1.10 million m$^3$ of Platte River water recharged the aquifer near Wood River through 5016 m$^3$ of the recharge basins during 1992, 1993 and 1994. This is equivalent to the quantity needed to
completely displace the ground water beneath 33.75 ha of the local primary aquifer. The water table rose rapidly in response to recharge during the early stage then leveled off as infiltration rates declined. The NO₃-N contamination improved from concentrations exceeding the maximum contaminant levels to those of drinking water quality. Infiltration rates decreased with time presumably because of clogging. Management practices such as scraping the basin floor, using a pulsed recharge strategy and maintaining low standing water heads in the basins appeared to reduce clogging, therefore enhanced infiltration.

Stable isotopes, anion concentrations and hydraulic gradients were used to delineate streamlines and mixing in ground water impacted by artificial recharge. The surface water fraction estimated from D/H ratios indicated that the recharged surface water completely displaced the ground water beneath the recharge basins from the regional water table at 7.60 m to 12.16 m below the land surface. Mixing occurred beneath the recharge structures in the lower portions of the aquifer (>12.16 m). At the end of the third recharge season, recharged surface water represented ~50% of the water in the deeper zone of the primary aquifer ~1000 m downgradient from the recharge basin.
ACKNOWLEDGEMENTS

I wish to express my deepest thanks to Dr. Roy F. Spalding, my advisor and chairman of my supervisory committee, for his constructive suggestions, keen interest, untiring patience, and encouragement throughout the course of study and my career in the Water Sciences Laboratory.

My sincere thanks are due to members of my supervisory committee, Drs. William Powers, Joseph Skopp, and Vitaly Zlotnik for their interest and suggestions on the projects and manuscripts. I also thank them for their excellent instruction in the classroom.

I thank Jay Bitner of the Upper Big Blue Natural Resources District for the background and operational information and for his effort on the simulation modelling. I am grateful for the sampling assistance of Russell Callan, Rod DeBuhr, Russell Gierhart (Upper Big Blue Natural Resources District) and Dan Clement (Central Platte Natural Resources District).

The staff in the Water Sciences Laboratory have always been very supportive and helpful. I thank Dan Snow for his effort to make everything go well and for our many constructive discussions. I am very grateful for the editorial assistance of Lorraine Moon, Lorraine has patiently polished the manuscripts and the dissertation. I thank Dave Cassada and Steve Monson for the herbicide analyses, Dave and Dan have also patiently solved all the computer problems. The field assistance of Mark Burbach and Jeff Toavs are also greatly appreciated. I also thank Dr. Glen Martin and Lesley Weir for their assistance in the stable isotope analysis.
I am also grateful for the helpful comments and suggestions of Prof. Mary Exner, Drs. Thomas Franti, and Sharon Widmer.

The York Ground Water Recharge Project was funded by the Upper Big Blue Natural Resources District and Ciba-Geigy. Wood River Ground Water Recharge Project was funded by the Central Platte Natural Resources District with funds from the US Bureau of Reclamation.

I am deeply thankful to my wife, Qingling, for her love and encouragement. I thank my sons, Paul and Darcy, for making our life more joyful.

To God I give my humble thanks.
# TABLE OF CONTENTS

**ACKNOWLEDGEMENTS** ........................................................................................................ i

**LIST OF FIGURES** ........................................................................................................ v

**LIST OF TABLES** ......................................................................................................... viii

**CHAPTERS:**

1 **INTRODUCTION** .......................................................................................... 1

2 **HERBICIDE PERSISTENCE AND MOBILITY IN RECHARGE LAKE WATERSHED IN YORK, NEBRASKA** ............ 7

   **Abstract** ................................................................................................... 7
   **Introduction** ............................................................................................ 8
   **Methodology** ....................................................................................... 12
   **Results and Discussion** ......................................................................... 22
   **Conclusions** .......................................................................................... 40
   **References** ............................................................................................ 44

3 **CHARACTERIZE ATRAZINE TRANSPORT FROM RECHARGE LAKE TO ADJACENT AQUIFER WITH A BROMIDE TRACER TEST** ................................................................................... 49

   **Abstract** ................................................................................................. 49
   **Introduction** .......................................................................................... 50
   **Methodology** ....................................................................................... 52
   **Results and Discussion** ......................................................................... 61
   **Summary** .............................................................................................. 69
   **References** ............................................................................................ 73

4 **EFFECTS OF ARTIFICIAL RECHARGE ON GROUND WATER QUALITY AND AQUIFER STORAGE RECOVERY** ...................... 76

   **Abstract** ................................................................................................. 76
   **Introduction** .......................................................................................... 77
   **Methodology** ....................................................................................... 79
   **Results and Discussion** ......................................................................... 86
   **Conclusions** ....................................................................................... 100
   **Literature Cited** .................................................................................. 102
5 STABLE ISOTOPE CHARACTERIZATION OF THE IMPACTS OF ARTIFICIAL GROUND WATER RECHARGE ........................................... 105

Abstract ............................................................................................... 105
Introduction ........................................................................................ 106
Methodology ..................................................................................... 108
Results and Discussion ....................................................................... 113
Conclusions ........................................................................................ 124
Literature Cited ................................................................................... 127

APPENDICES:

A. Status of Manuscripts ............................................................... 130
B. Herbicide concentrations at York Ground Water Recharge Project 131
C. Bromide concentrations at York Ground Water Recharge Project . 158
D. Multilevel wells screen elevations at York Ground Water
   Recharge Project ............................................................................. 165
E. Sediment fraction analysis at York Ground Water Recharge Project 166
F. NO$_3$-N concentration at Wood River Ground Water Recharge Project 174
G. Water table at Wood River Ground Water Recharge Project .......... 189
H. Isotopic compositions at Wood River Ground Water Recharge Project 193
LIST OF FIGURES

Chapter 1. Introduction

Figure 1. Outline of the dissertation ................................................. 2

Chapter 2. Herbicide Persistence and Mobility in Recharge Lake Watershed in York, Nebraska.

Figure 1. Degradation pathways of atrazine to hydroxyatrazine, deethylatrazine (DEA), and deisopropylatrazine (DIA) and of cyanazine to DIA. ........ 10

Figure 2. Well and surface water sampling locations at the York Groundwater Recharge site. ................................................................. 13

Figure 3. Pathways of herbicide fate and transport in the Beaver Creek watershed. .................................................................................. 23

Figure 4. Precipitation (a), average herbicide concentrations (b) and D^2R in runoff events at the York Ground Water Recharge site in 1994. ... 25

Figure 5. Atrazine, DEA, DIA, DAR, and D^2R in the first runoff event on June 22, 1994. ................................................................. 29

Figure 6. Herbicide concentrations (a), DAR and D^2R (b) in Recharge Lake during summer of 1993. .................................................. 30

Figure 7. Herbicide concentrations (a), DAR and D^2R (b) in Recharge Lake during summer of 1994. .................................................. 31

Figure 8. Measured and adjusted atrazine and DEA concentrations in Recharge Lake during summers of 1993 (a) and 1994 (b). ......................... 33

Figure 9. Ground water atrazine concentrations at two depths in well M1, close to Recharge Lake during summer of 1994. .......................... 41

Chapter 3. Characterize Atrazine Transport from Recharge Lake to Adjacent Aquifer with a Bromide Tracer Test.

Figure 1. Well and surface water sampling locations at the York Ground Water Recharge Project. The enlarged portion of Recharge Lake represented the bromide spiking area. ........................................ 53
Chapter 4. Effects of Artificial Recharge on Ground Water Quality and Aquifer Storage Recovery.

Figure 1. Location map. 80

Figure 2. Wood River ground water recharge site profile. 81

Figure 3. Total water pumpage (a), infiltration rates (b), and water table changes (c) at 12.16 m downgradient from the basin B (PZ9) during 1992, 1993, and 1994 recharge seasons. 87

Figure 4. Initial water table, water table increases resulted from AGWR and precipitation at the end of third recharge season. 92

Figure 5. The NO₃-N concentrations at 12.16 m downgradient from the basin B (PZ9) during 1992, 1993 and 1994 recharge season. 93

Figure 6. The NO₃-N concentrations at 12.16 m upgradient from the basin A (PZ8) during 1992, 1993 and 1994 recharge season. 96

Figure 7. Short term variations in NO₃-N concentrations at depths (a) 9.73 m, (b) 12.16 m, and (c) 19.15 m of the piezometers that transect the recharge basins during the 1994 recharge season. 98

Figure 8. Atrazine concentrations at 12.16 m downgradient from the basin B (PZ9) during 1992, 1993 and 1994 recharge season. 99


Figure 1. Progressive recharge impact on ground water beneath the recharge basins. Recharge activity started on April 6, 1994. Shaded area with date
showed SWF≥50%. Vertical scale was exaggerated. ............................. 114

Figure 2. Seasonal variations in deuterium composition of surface water and nonimpacted local ground water at the site during 1992, 1993 and 1994 recharge seasons. .......................................................... 118

Figure 3. Relationship between deuterium and oxygen-18 compositions of nonimpacted local ground water, impacted ground water, and surface water. Values in the upper circle represented the nonimpacted local ground water; middle circle represented the samples resulted from the mixing between surface water and ground water; and lower circle included the surface water and ground water samples that are almost completely displaced by the recharged surface water. ......................................................... 120

Figure 4. Surface water fraction (SWF), NO₃-N and sulfate concentrations during 1992, 1993, and 1994 recharge seasons. ................................. 122
LIST OF TABLES

Chapter 2. Herbicide Persistence and Mobility in Recharge Lake Watershed in York, Nebraska.

Table 1. Percentage of acreage of herbicide usage, application rates, total annual application on corn, grain sorghum and soybean acres in the York Recharge Basin Drainage Area ................................................................. 15

Table 2. Estimated total percentage of herbicides lost to runoff during growing seasons ................................................................................................................ 24

Table 3. Average herbicide degradation and dissipation half-lives in Recharge Lake estimated from the exponential decay equation, published surface water half-lives, and solubility. Correlation coefficient given in parentheses. ... 35

Table 4. Average NO$_3$-N, herbicide, DAR, and D$_2$R in ground water in the YGWRP drainage basin. The number in parenthesis after the well ID is the total number of the samples used to compute the average. .............................. 37

Chapter 3. Characterize Atrazine Transport from Recharge Lake to Adjacent Aquifer with a Bromide Tracer Test.

Table 1. Modeling stress periods and Recharge Lake infiltration. The information was surveyed by the Upper Big Blue NRD (Bitner, personal communication). .......................................................... 59

Table 2. Operational pumping wells in the York Ground Water Recharge Lake area. Layer, column, and row were used in the finite difference grid design for simulation models. The information was surveyed by Upper Big Blue NRD (Bitner, personal communication) ........................................... 60

Table 3. Bromide tracer concentrations and arrival times .................................. 63

Chapter 4. Effects of Artificial Recharge on Ground Water Quality and Aquifer Storage Recovery.

Table 1. The NO$_3$-N concentrations at the end of the third recharge season (June 1, 1994) at peripheral piezometers and piezometers that transect the recharge basins in the local ground water flow direction. .......................... 95

Table 1. Vertical hydraulic gradients at the Wood River Ground Water Recharge site during 1994 recharge season (recharge began on April 7). Negative values indicate ground water moving upward. .................. 115

Table 2. Horizontal hydraulic gradients at the Wood River Ground Water Recharge site during 1994 recharge season. Negative values represent ground water moving in upgradient direction. .......................... 116
Chapter 1

INTRODUCTION

The research forming the basis of this dissertation focuses on two ground water recharge projects, namely the Wood River Ground Water Recharge Project (WRGWRP) and the York Ground Water Recharge Project (YGWRP). Both of these demonstration projects were implemented as part of the U.S. Bureau of Reclamation's (USBR) High Plains Ground Water Recharge Demonstration Program. The Central Platte Natural Resources District (NRD) and the Upper Big Blue NRD are the local sponsors for the projects. For the project duration funding was received from the USBR and Ciba-Geigy Corporation through the local NRDs.

This dissertation is presented as a series of four manuscripts based on the two projects (Fig. 1). The manuscripts' status and authorship, field measurements and laboratory determinations are documented in the appendices.

In chapter two, herbicide behavior is interpreted in a watershed system with data collected from runoff, Recharge Lake, and ground water which was influenced by agriculture and lake seepage. The objectives of this research were: 1) to document the occurrence of herbicides in agricultural runoff impacting a recharge basin; 2) to estimate the persistence of herbicides in Recharge Lake; and 3) to relate the distribution of herbicides in ground water to input sources. Maximum atrazine inputs to Recharge Lake occurred in May and June runoff events and resulted in atrazine concentrations of 36 and 17 μg L⁻¹ in 1993 and 1994 respectively. About 0.28% and 0.19% of total applied...
Figure 1. Outline of the dissertation.
atrazine was lost to runoff in 1993 and 1994, respectively. The deethylatrazine (DEA) to atrazine molar ratio (DAR) decreased rapidly over a period of several hours in runoff samples, which is consistent with inputs from recently atrazine treated soil. Atrazine concentrations in Recharge Lake decreased exponentially with time. Degradation half-lives were 237 d ($r=0.93$) in 1993 and 209 d ($r=0.91$) in 1994. Adjusted DEA concentrations in Recharge Lake remained relatively constant, providing no direct evidence for biotic degradation, and suggesting that abiotic degradation of atrazine to hydroxyatrazine was the most likely major degradative pathway in Recharge Lake.

Chapter three examines the interaction between Recharge Lake and adjacent aquifer with bromide and the simulated atrazine distribution. Maximum bromide concentrations obtained in the nearby aquifer represented only 27% of the initial concentration in Recharge Lake. The low detected concentrations might be due to the low infiltration rates and followed by dilution with the ground water. Breakthrough times varied considerably at different depths of the same horizontal distance from Recharge Lake, indicating a highly heterogenous aquifer beneath Recharge Lake and adjacent area. The lake infiltration rates declined with time due to biofouling accumulation of organic material on the bottom of Recharge Lake. Hydraulic conductivities (K) of the adjacent aquifer were estimated with the Kozeny-Carmen equation based on grain size distribution and ranged from 1 to 390 ft/day. The aquifer was divided into three layers with an averaged K of 128 ft/day for top layer (25 ft thickness), 162 ft/day for layer 2 (26 ft), and 29 ft/day for layer 3 (18 ft). A pumping test at 1000 ft downgradient from Recharge Lake with a pumping well screened from 44 ft to 70 ft resulted in a K of 136 ft/day.
These parameters were used to calibrate ground water flow and solute transport models used to simulate atrazine distribution in the adjacent aquifer. A simulated atrazine plume dispersed radially from Recharge Lake with a strong southeast movement and simulated concentrations agreed favorably with the measured concentrations.

Chapter four, Effects of Artificial Recharge on Ground Water Quality and Aquifer Storage Recovery, discusses the impacts of the WRGWRP during 1992, 1993 and 1994. The objectives of this research were to document improved ground water quality and increased quantity from artificial ground water recharge (AGWR) and to determine beneficial operation and management strategies. A total of 1.10 million m$^3$ of Platte River water recharged the aquifer through 5016 m$^2$ of the recharge basins near Wood River, Nebraska during 1992, 1993 and 1994. This is equivalent to the quantity needed to completely displace the ground water beneath 33.75 ha of the local primary aquifer. The water table at the site rose rapidly in response to recharge during the early stage then leveled off as infiltration rates declined. Both NO$_3$-N and atrazine contamination dramatically improved from concentrations exceeding the maximum contaminant levels to those of drinking water quality. Resultant ground water quality improvement and aquifer storage increase from the artificial recharge were measured at ~1000 m downgradient and ~600 m upgradient from the recharge basins. Constant infiltration rates were not sustained in any of the three years, and the rate always decreased with time presumably because of clogging. Scraping the basin floor increased infiltration rates. Other management practices, such as using a pulsed recharge strategy to create dry and
wet cycles and maintaining low standing water heads in the basins appeared to reduce microbial growth resulted in more sustainable infiltration rates.

In chapter five, stable isotopes of deuterium and oxygen-18 of surface and ground water, together with anion concentrations and hydraulic gradients, were used to interpret mixing and flow in the ground water impacted by artificial recharge. The surface water fraction (SWF), the percentage of surface water in the aquifer impacted via recharge, was estimated at different locations and depths from measured D/H ratios during the 1992, 1993 and 1994 recharge seasons. Recharged surface water completely displaced the ground water beneath the recharge basins from the regional water table at 7.60 m to 12.16 m below the land surface. Mixing occurred beneath the recharge structures in the lower portions of the aquifer (>12.16 m). Approximately 12 m downgradient from the recharge basin, the deeper zone (19.15 m depth) of the primary aquifer was displaced completely by recharged surface water within 193, 45, and 55 days in 1992, 1993 and 1994, respectively. At the end of the third recharge season, recharged surface water represented ~50% of the water in the deeper zone of the primary aquifer ~1000 m downgradient from the recharge basin. A classic asymmetrical distribution of recharged surface water resulted from the recharge induced horizontal and vertical hydraulic gradients. The distribution and breakthrough times of recharged surface water obtained with stable isotopes concurred with those of major anions.
Future Researches

This research suggests abiotic degradation of atrazine to hydroxyatrazine is the most likely major degradative pathway in Recharge Lake. Research is needed to determine the accumulation rate of hydroxyatrazine (HA) in the lake bottom and conduct experiments to increase HA degradation. HA is the only major dehalogenated degradate that is considered nontoxic. Drs. Spalding and Cai, both at the Water Sciences Laboratory, have written a proposal for method development to analyze hydroxyatrazine in the sediment, which has an excellent chance of being funded.

More research is needed to identify effective methods to control clogging in the recharge basins and to enhance efficacy of recharge. Alternating biological growth conditions, such as introducing a disinfectant chlorine into the basins, may be effective in controlling the biological growth in recharge basins. Improved design of the settling basin may be tested to reduce the solid particles entering the recharge basins.
Chapter 2
Herbicide Persistence and Mobility in Recharge Lake Watershed in York, Nebraska

ABSTRACT

Reports of the detection of elevated levels of herbicides in surface water and ground water have created increasing concern in the cornbelt in the USA. Herbicide behavior is interpreted in a watershed system with data collected from runoff, Recharge Lake and ground water influenced by agriculture and lake seepage. The York Ground Water Recharge Project was constructed on a tributary of Beaver Creek which drains a watershed of 3,327 ha of primarily row-cropped heavily irrigated farmland. The estimated average runoff is 1.48x10⁶ m³ yr⁻¹ under a precipitation norm of 635 mm yr⁻¹. Maximum atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) inputs to Recharge Lake occurred in May and June runoff events and resulted in atrazine concentrations of 36 and 17 µg L⁻¹ in 1993 and 1994 respectively. Deethylatrazine (2-chloro-4-amino-6-isopropylamino-s-triazine; DEA), deisopropylatrazine (2-chloro-4-ethylamino-6-ethylamino-s-triazine; DIA), alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide), cyanazine (2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylpropionitrile), and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide) were also present in runoff, Recharge Lake and the ground water samples. About 0.28% and 0.19% of total applied atrazine was lost to runoff in 1993 and 1994, respectively. The DEA to atrazine molar ratio (DAR) decreased rapidly over a period of several hours in runoff samples, which is consistent with inputs