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**CHEMICAL, ISOTOPIC, AND HYDROGEOLOGIC INVESTIGATIONS OF AN
AGRICULTURALLY IMPACTED AREA, NOTTAWA CREEK
WATERSHED, CALHOUN COUNTY, MICHIGAN**

by

Gerald A. Unterreiner

**A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Geosciences**

**Western Michigan University
Kalamazoo, Michigan
April 2002**

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THE GRADUATE COLLEGE
WESTERN MICHIGAN UNIVERSITY
KALAMAZOO, MICHIGAN

Date January 25, 2002

WE HEREBY APPROVE THE DISSERTATION SUBMITTED BY

Gerald A. Unterreiner

ENTITLED Chemical, Isotopic, and Hydrogeologic Investigations of an Agriculturally

Impacted Area, Nottawa Creek Watershed, Calhoun County, Michigan

AS PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy

Geosciences

(Department)

Geology

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**CHEMICAL, ISOTOPIC, AND HYDROGEOLOGIC INVESTIGATIONS OF AN
AGRICULTURALLY IMPACTED AREA, NOTTAWA CREEK
WATERSHED, CALHOUN COUNTY, MICHIGAN**

Gerald A. Unterreiner, Ph.D.

Western Michigan University, 2002

A 4 km² agricultural area within the somewhat poorly drained Nottawa Creek Watershed, south central Michigan, was investigated to help understand transport and transformation processes of nutrients and herbicides to surface water. Geology of the study area is comprised of a thin glacial drift cover overlying shale bedrock. A one layer, two-dimensional numerical triangular finite element groundwater flow model was developed to evaluate regional groundwater flow. Selected horizontal hydraulic conductivities ranged from 3×10^{-3} m/day to 107 m/day. Field-scale infiltration modeling with the computer program GLEAMS, substantiated with water level measurements, suggest significant recharge events occur during summer, as well as fall and spring. Depth to groundwater varied from about 1.5 to 7.6 meters.

Geochemical data were collected for 12 sampling events over 22 months, from December 1999-September 2001, for Nottawa Creek surface water, 9 water table monitoring wells, 4 domestic drift wells, and 8 tile drains. Tile drains were a major contributor of nitrogen and phosphorus to surface water. Despite this, Nottawa Creek nutrient concentrations were consistently low. Tritium results from the two

streambed wells, which were uncontaminated with nitrate, indicate groundwater discharging into Nottawa Creek is post-bomb water.

Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ from nitrate from most wells and tile drains suggest that field applied synthetic fertilizer, composted manure, and liquid manure is transformed or not present. Wells adjacent to an animal waste lagoon and a compost pile exhibit a denitrification or animal waste isotopic signature.

Concentrations detected by immunoassay, GC/MS, and LC/MS are reported for triazine and acetamide herbicides. Herbicides and degradation products are transported to surface water by tile drains. Low or non-detect herbicide concentrations in monitoring wells suggest significant degradation or retardation. Immunoassay test results suggest metolachlor ESA was detected in wells, rather than metolachlor.

Herbicide testing implied a seasonal concentration detection peak occurring in June-July, which subsequently tapered off dramatically. Low early fall concentrations were substantiated by GC/MS and LC/MS methods in which only metolachlor and alachlor metabolites were detected in streambed wells and Nottawa Creek surface water. Atrazine and other triazine herbicides were not detected for the LLD of $0.05\ \mu\text{L}$.

ACKNOWLEDGMENTS

This dissertation is dedicated to the late Ms. Lauren Hughes of Western Michigan University's Groundwater Education in Michigan Center. Lauren was a scientist and an ambassador for the GEM Center. There will always be a special place in my heart for Lauren. Thank you.

The author would also like to express gratitude to others who have contributed time and support in the preparation of this dissertation. The writer wishes to thank the following:

Dr. Alan E. Kehew for acting as my advisor and mentor.

Dr. R.V. Krishnamurthy and Dr. Duane R. Hampton of Western Michigan University and Dr. Joseph G. Meert of the University of Florida for serving on my committee.

Mr. Daniel Kesselring, District Conservationist of the Natural Resources Conservation Service.

Mr. Robert Pigg of the Michigan Department of Agriculture.

Ms. Sue Nap of Western Michigan University's Groundwater Education in Michigan Center.

Ms. Jenny Molloy and Ms. Dawn Hartig of the Michigan Department of Environmental Quality.

Ms. Betty Scribner of the of the United States Geological Survey.

Acknowledgments-Continued

Andy Kozlowski, Brian Bird, Dale Werkema, and Shannon Wong of Western Michigan University's Geosciences Department for technical assistance.

Western Michigan University, the United States Environmental Protection Agency, Michigan Department of Environmental Quality, Michigan Department of Agriculture, and Geological Society of America for funding portions of research for this dissertation.

The gracious citizens residing in the Nottawa Creek Watershed for kindly allowing me to take samples of their well water.

Lastly, but most importantly, my lovely wife.

Gerald A. Unterreiner

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CHAPTER I

INTRODUCTION

A report by the United States Geological Survey (USGS, 1999) on their National Water-Quality Assessment Program (NAWQA) indicated nonpoint source contamination of water resources may be a nationwide problem. Nonpoint source degradation of water resources occurs as a result of the combination of many contamination sources, as opposed to pollution originating from a distinct and identifiable point source (Kehew, 2001; USGS, 1999). While point sources are regulated under the National Pollutant Discharge Elimination System (NPDES), it is much more difficult to quantify and regulate sources of nonpoint pollution (USGS, 1999). A wastewater treatment facility is an example of a point source, while agricultural and urban areas, as well as the atmosphere, are nonpoint sources (USGS, 1999). To cite an instance, the USGS (1999) in a NAWQA report, estimated that about 90% of nitrogen and 75% of phosphorus originated from nonpoint sources with the remaining percentages derived from point sources. These results are from 20 major river basins and aquifer systems within various geographic regions across the nation. The report also stated at least one pesticide was found in almost every water and fish sample collected from streams and in about one-half of all shallow (less than 30 m) wells sampled. Insecticides were detected most often in urban streams while

herbicides were the most common pesticide detected in agricultural areas.

Degradation of water quality commonly occurs in agricultural and urban areas because of land application of nutrients and/or pesticides (Mueller et al., 1995; Korom, 1992; USGS, 1999). Nitrogen (N) and phosphorous (P) are essential plant and animal nutrients but may degrade water quality at elevated concentrations (USGS, 1999). Plant nutrients are typically applied in the form of synthetic fertilizer in urban areas, and manure, compost, and/or synthetic fertilizer on agricultural fields. Pesticides are generally grouped into the two broad categories of herbicides and insecticides with regard to control of weeds and insects, respectively. Pesticides are potentially harmful to human health and aquatic environments at elevated concentrations (USGS, 1999).

Contamination of water resources occurs when rain falls or snow melts, as water carries pollutant by-products from the land into surface water and groundwater. Some pollutants break down in the environment, or are diluted, to insignificant levels. However, other pollutants may accumulate to detrimental levels affecting drinking water supplies, aquatic habitat, and recreational activities.

This is a case study involving nonpoint source pollution, which examines the impact of agricultural activities on the quality of surface water and groundwater. This dissertation investigates the contribution of agricultural land to nonpoint source water degradation within the Nottawa Creek Watershed, Calhoun County, Michigan (Figure 1). The study takes place on and near a private farm. The predominantly agricultural (68% of land use) Nottawa Creek Watershed encompasses 240 km² in south-central

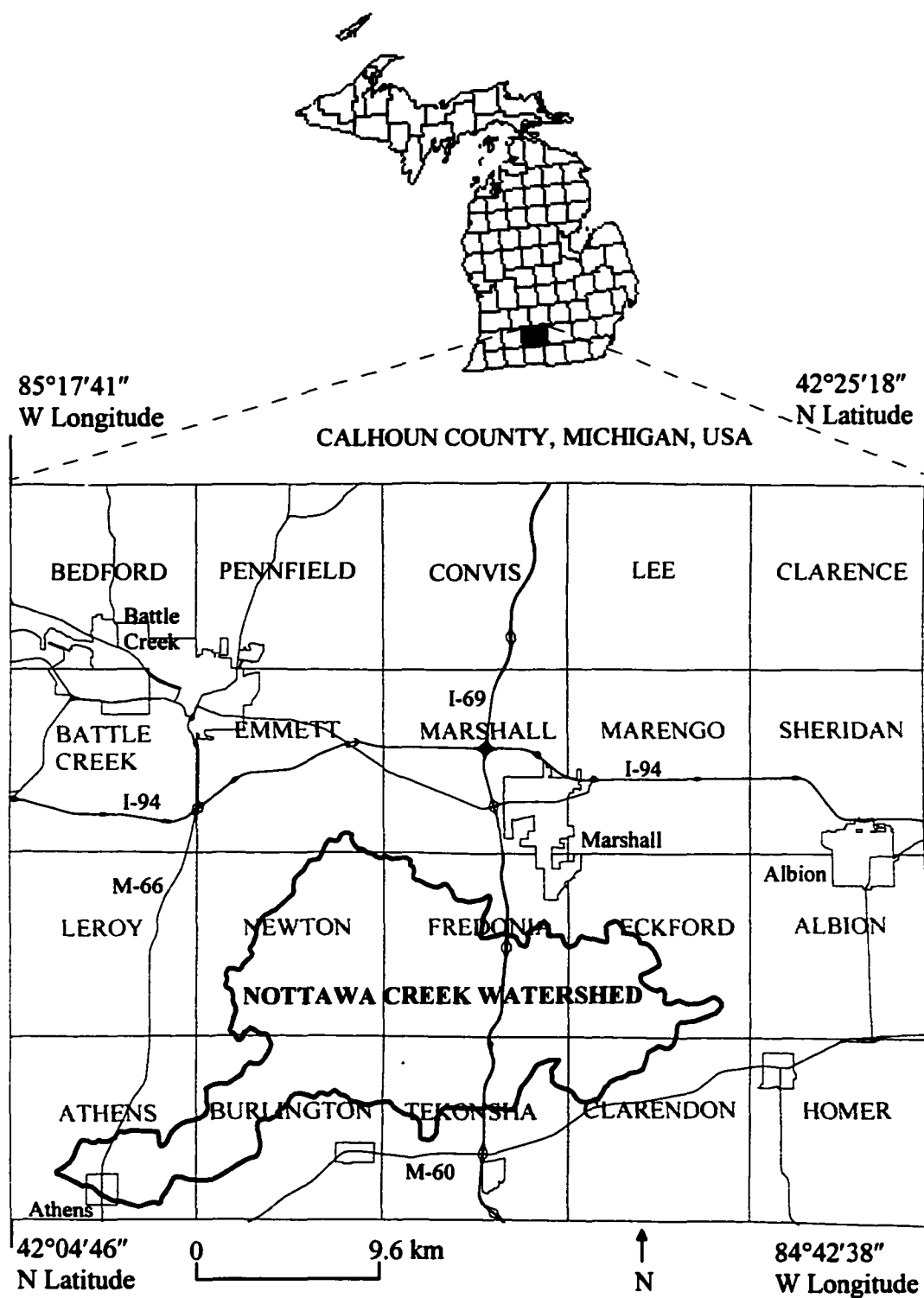


Figure 1. Locality Map with Townships (Base Map Data from MDNR MIRIS Files).

Michigan and is a sub-watershed of the St. Joseph River Basin. The St. Joseph River flows into Lake Michigan. The St. Joseph River Watershed is not included in the more than 50 major river basins and aquifer systems of NAWQA study units (USGS, 1999).

This study of the Nottawa Creek Watershed was partially funded by a grant from the United States Environmental Protection Agency (USEPA) under Section 319 of the Clean Water Act. The grant was administered through the Michigan Department of Environmental Quality (MDEQ) and the Western Michigan University (WMU) Groundwater Education in Michigan (GEM) Center. This case study of groundwater/surface water interaction is part of a Comprehensive Watershed Management Plan entitled the "Nottawa Creek Watershed Project" (Calhoun Conservation District, 1998).

The Nottawa Creek Watershed Project, a wide-ranging study with many contributors, initially arose out of concern from various governmental and community groups (Calhoun Conservation District, 1998). The organizations desired to know what impact agriculture, recreational activities, increasing population growth, and economic expansion might have on the watershed. For instance, there is some concern the rural setting of the watershed may change significantly in the future. The headwaters of the Nottawa Creek Watershed are near the junction of interstate highways I-94 and I-69, a natural corridor for economic growth and expansion. In addition, considerable development has recently taken place along the southeastern edge of the city of Battle Creek.

Scope of the Problem

Groundwater contamination in agricultural watersheds is well documented (Mueller et al., 1995; USGS, 1999). In fact, this study of the Nottawa Creek Watershed arose in part because groundwater contamination has occurred within the watershed. For example, the Village of Athens, located near the mouth of the watershed, recently (~1990) ceased pumping the long-standing community shallow groundwater supply well because of chronic nitrate (NO_3^-) contamination of ~19 mg/L (milligrams per liter) as NO_3^- -N (Jerry Snodderly, personal comm., 1999).

The USEPA (1995) has established a health-based drinking water standard for NO_3^- -N of 10 mg/L. While nitrate is ordinarily not considered to be a health risk for healthy adults, ingestion of nitrate-contaminated water can cause infant methemoglobinemia (i.e., blue-baby syndrome; Grant et al., 1996). This is a potentially fatal condition due to low oxygen levels in the blood as ingested nitrate is converted to nitrite and normal hemoglobin is converted to methemoglobin (Spalding and Exner, 1993). Infants under 4 months of age lack the enzyme necessary to correct this condition (Mueller and Helsel, 1996).

Another health effect connected with ingestion of nitrate-contaminated water is spontaneous abortion in laboratory animals and livestock (Grant et al. 1996; Sund et al., 1957). Moreover, in a study conducted in rural northeastern Indiana, Grant et al. (1996) reported a possible association between ingestion of nitrate-contaminated drinking water from private wells and miscarriage in humans.

Although N is essential to plant and animal life, high concentrations of N can be harmful to aquatic life. The removal of oxygen from water in streams can adversely affect fish (Mueller and Helsel, 1996). This can be represented by the following reaction as ammonium (NH_4^+) is naturally converted to NO_3^- .



In addition, elevated concentrations of N and P can stimulate eutrophication in water bodies. The limiting nutrient for excessive plant growth in saltwater and coastal waters is N, whereas it is P for freshwater (USGS, 1999). The USEPA has recommended total phosphates should not exceed 0.05 mg/L (as P) in a stream at a point where it enters a lake or reservoir (Mueller and Helsel, 1996). Furthermore, total P should not exceed 0.1 mg/L in streams to prevent nuisance plant growth (USGS, 1999).

Water quality standards and guidelines for pesticides may only partially address potential risks to humans and aquatic life (USGS, 1999). The situation is complicated as pesticide breakdown products, for which there is little health based research, are frequently found more often in groundwater samples than their parent compounds (USGS, 1999). In addition there is little health based research on combinations of compounds (USGS, 1999).

Herbicides are pesticides that are used to kill vegetation and pose the greatest threat to water quality in agricultural areas because they are applied in a greater

volume than other pesticides. In fact, Wauchope et al. (1994) reported herbicides account for 75% of the pesticide use in U.S. agriculture.

Importance of the Study

This study of the Nottawa Creek Watershed is important because the citizenry is 100% dependent on groundwater as a drinking water supply (WMU, 1992). Consequently, well water that is clean and requires no purification treatment is a precious resource.

Water quality studies in rural areas are important because toxic chemicals frequently provide little warning of their presence in drinking water and may pose a serious threat to health that is often not readily apparent to those affected (Heath, 1983; Mueller and Helsel, 1996; Harr, 1996). Unlike public water systems, whose drinking water is regulated by the USEPA, private well operators alone are responsible for having their water tested to ensure it is fit for drinking.

Economic considerations are also an important aspect concerning well water quality. Financial burdens have been placed on small communities, such as Athens, which have had to abandon shallow NO_3^- contaminated wells in favor of potable groundwater from deeper formations, in order to comply with the NO_3^- requirement of the Safe Drinking Water Act. In addition to increased energy costs, water obtained from the deeper wells is mineralized and must be treated for iron and manganese.

A concern of importance locally, as well as regionally in regard to large

municipalities that rely on groundwater, is that nitrate-rich recharge waters may simply not had enough time to reach deeper formations (Fenelon and Moore, 1998). For example, a study of the Schoolcraft Aquifer in Kalamazoo County, Michigan by Kehew et al. (1996) noted nitrate contamination limited to the shallow flow system, defined as wells screened above 30 m below land surface. Wells screened within the shallow flow system above 10 m below land surface had the highest NO_3^- -N concentrations of greater than 30 mg/L. The Schoolcraft Aquifer has recently been found to be contaminated by NO_3^- -N (50-80 mg/L) at depths up to 23 m below ground surface (Hyndman et al., 2000). Kehew et al. (1996) reported a pump test from a well screened in the deep flow system implied high pumping rates could increase the vertical gradient of the natural flow system and induce nitrate contamination from the shallow flow system to the deep one.

Time may be a crucial component regarding nitrate-rich recharge waters since large scale application amounts of nitrogen fertilizers generally did not become widespread until the 1940s (Mueller and Helsel, 1996). This is a significant consideration for areas, similar to the Nottawa Creek Watershed, which are 100% dependent on groundwater as a drinking water supply.

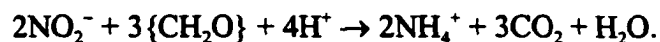
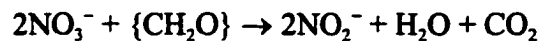
Case studies are important in that they add to the body of knowledge to assist in the refinement of best management practices (BMPs). Improved understanding of N source loading may lead to BMPs that will allow with time natural remediation of NO_3^- contaminated shallow aquifers. Additionally, watershed stakeholders in similar terrain may also benefit from lessons learned in order to prevent shallow groundwater

contamination from occurring.

This study may assist the citizenry of the Nottawa Creek Watershed, and other similar watersheds, with regard to specific fertilizer applications in conjunction with hydrogeologic conditions. Hydrogeology is crucial because heavier N source loading on particular fields may result in natural degradation with less susceptibility to groundwater NO_3^- contamination than others. For example, it has been noted (Fenelon and Moore, 1998; Korom, 1992) that under reducing conditions, NO_3^- may be biochemically converted to N gas by denitrification or biochemically reduced to ammonia. Denitrification can be represented by the following reaction, where $\{\text{CH}_2\text{O}\}$ represents fixed organic carbon (Manahan, 1993).



NO_3^- can be biochemically reduced to ammonia as represented by the following reactions:



Dissimilatory nitrate reduction to ammonia competes with denitrification and may be favored when dissolved oxygen concentrations are low (≤ 0.3 mg/L), organic carbon (e^- donor) supplies are not limited, and nitrate (e^- acceptor) concentrations are low

(Fenelon and Moore, 1998; Korom, 1992).

In situations where livestock and plant farming are performed in conjunction, contamination prevention may simply become an issue of where to spread the excess nutrient wastes. Isotopic study of the behavior of N fertilizer in this situation may possibly be helpful in assessing groundwater contamination, because nitrogen fertilizers and biologically mediated transformation processes can be investigated using isotopic ratios of nitrogen (USGS, 2000).

Hydrologic inputs are also of important consideration in this study. Hydrologic studies in temperate areas, such as south-central Michigan, have demonstrated groundwater is a major component of streamflow (Holtschlag, 1997). Therefore, the nutrient and pesticide load to surface water from shallow groundwater is a critical component in the management of local and regional ecological systems.

In summary, this study may be helpful to watershed stakeholders concerned with maintaining or attaining water quality standards. It is hoped this study assessing groundwater/surface water interaction will aid in these efforts.

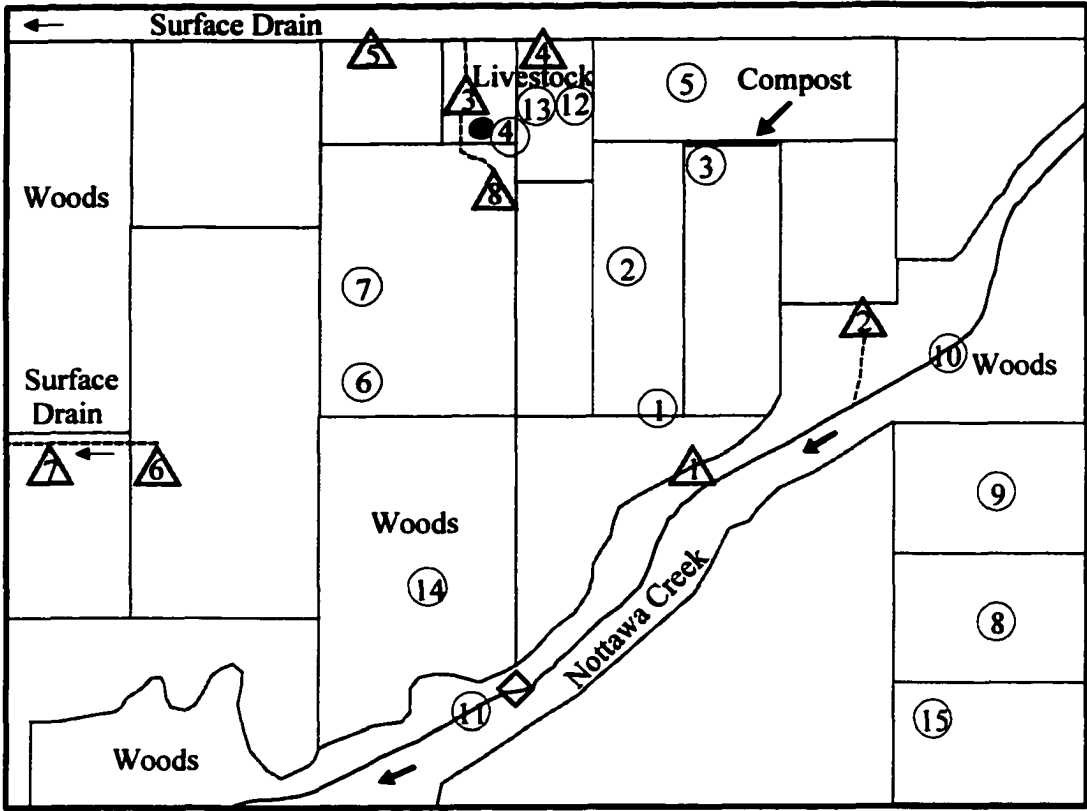
Statement of Purpose

Sustainability of water resources, in regards to water quality, may best be met by conducting a complete analysis of the hydrologic system of interest (Alley et al., 1999; Hendry et al., 1983). To this end, water quality analysis was guided by compiling physical, chemical, and hydrologic data.

This research characterizes relationships between groundwater flow systems and Nottawa Creek by utilizing an integrated assessment of surface water, groundwater, and tile drain effluent. A farm and surrounding area (Figure 2) were chosen as a case study site for the Nottawa Creek Watershed Project and serves as the primary research focus for the dissertation. The area was chosen for its locale near the mouth of the watershed, where the shallow aquifer seems particularly sensitive to contamination. In addition, the farm is ideal for study because of extensive records kept by the individual farming operation as well as the operators' cooperative nature. In fact, the private enterprise is considered one of the best run farms in the watershed (Dan Kesselring, personal comm., 1999). The farm may serve as a "model" for similar type farms and agricultural areas throughout the Nottawa Creek Watershed.

The research is part of a comprehensive study of surface water/groundwater interaction at a watershed scale. In this sense, Nottawa Creek surface water quality sampled at one location cannot be distinguished from upstream components. As previously stated, a practical objective of this dissertation research is to provide information, which may assist Nottawa Creek Watershed stakeholders in refinement of BMPs. In addition, results of the study may aid communities of the watershed in directing growth to minimize negative impacts on the land and water. Finally, this study may be helpful to stakeholders and decision makers, in similar environments, concerned with maintaining or attaining water quality standards and guidelines.

Particular scientific methods were addressed to meet these concerns and goals. The research is described in the dissertation in several segments with the following



EXPLANATION

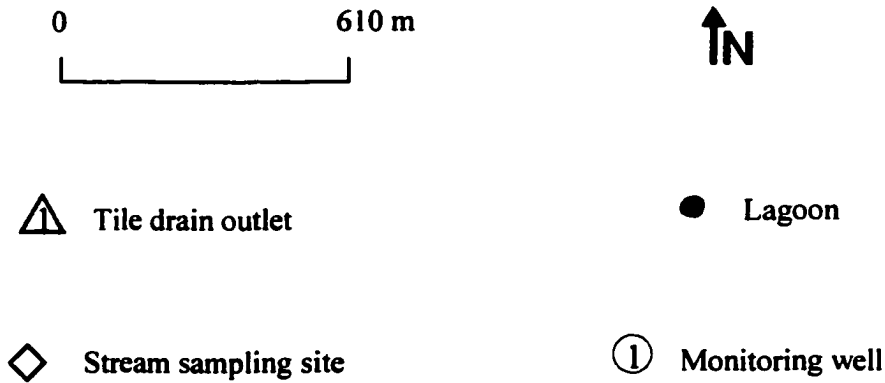


Figure 2. Schematic of the Study Area (Modified from USDA Photographs).

headings: (1) Comparison of field scale model monthly infiltration rates to estimated basin recharge; (2) A BASIC triangular finite element groundwater flow model; (3) Spatial and temporal geochemistry trends in groundwater, agricultural drains, and surface water; (4) Evaluating shallow groundwater vulnerability with environmental isotopes; (5) Tracing nitrogen sources with isotope fractionation of nitrate-nitrogen and nitrate-oxygen; (6) Sediment grain size analysis and in situ denitrification potential, and (7) Field scale evaluation of the fate of agrichemicals with the immunoassay test.

The conclusions and recommendations section of the dissertation comprises an integrated assessment of the above mentioned investigative techniques. In addition, research results are compared with other information resources in the watershed (Kehew et al., 1999a; Dannemiller and Baltusis, 1990) to formulate a general water quality report and recommendations for the Nottawa Creek Watershed. Unpublished chemical and isotopic data (Kehew et al., 1999a) from water samples of 35 domestic wells (13 glacial drift and 22 bedrock) and several surface water sites are included in this discussion. These samples were collected from scattered locations throughout the watershed and so, although not conclusive, represent trends in water quality by area. Dannemiller and Baltusis (1990) cite chemical and isotopic data for one deep bedrock well within the watershed. In addition, Dannemiller and Baltusis (1990) report chemical and isotopic data from several deep bedrock wells just outside of the watershed boundaries as part of the USGS Michigan Basin Regional Aquifer-System Analysis.

CHAPTER II

LITERATURE REVIEW AND RESEARCH

Previous Studies

A landmark study describing the glacial geology of Michigan, including the dissertation study area, is presented by Leverett and Taylor (1915). A detailed report of the glacial geology and depth to bedrock for the Athens area is given in Kozlowski (1999).

There have been several water quality studies conducted of the Nottawa Creek Watershed area. Foremost is the study by Moser and Passero (1990) which aptly describes the geology and aquifers of Calhoun County. A more colorful version of this summary is depicted in a Western Michigan University publication (WMU, 1992). Kehew et al. (1999a) present an analysis of unpublished chemical and isotopic data from water samples of 35 domestic wells (13 glacial drift and 22 bedrock) and several surface water sites collected from disseminated locations throughout the watershed. Chowdhury (1999) describes a computer model of groundwater vulnerability to contamination from surface sources utilizing water chemistry of these samples (Kehew et al., 1999a). Chemical and isotopic data for one bedrock well within the watershed is reported by Dannemiller and Baltusis (1990). Holtschlag

(1997) gives a generalized estimate of groundwater recharge rates for the Nottawa Creek Drainage Basin.

Several local studies also are of related significance to this research. Kehew et al. (1996) present a comprehensive assessment of a shallow aquifer impacted by agricultural contamination, southwestern Michigan. A study of isotopic variations in precipitation for stable isotopes of oxygen and hydrogen for the Great Lakes region is documented in Machavaram and Krishnamurthy (1995). Nascimento et al. (1997) cite concentrations and isotope ratios of dissolved inorganic carbon in denitrifying environments from nearby Cass County. Kehew et al. (1998) describe hydrogeochemical interaction between a wetland and an unconfined glacial drift aquifer, southwestern Michigan. As previously stated, Dannemiller and Baltusis (1990), report chemical and isotopic data from several deep bedrock wells just outside of the watershed boundaries. Atekwana and Krishnamurthy (1998) describe seasonal variations of dissolved inorganic carbon and $\delta^{13}\text{C}$ of surface waters from adjacent Kalamazoo County. Lastly, an account of the complex glacial geology of the interlobate region is given by Kehew et al. (1999b).

Geology of the Nottawa Creek Watershed

Glacial Geology

Pleistocene glacial sediments underlie the Nottawa Creek Watershed (Moser

and Passero, 1990). Glacial ice extended into Michigan several times during the last 500,000 years and was followed by warmer periods and erosion following retreat of the ice (Leverett and Taylor, 1915; Dorr and Eschman, 1970). Evidence in Michigan of glacial deposits is scant for all but the most recent glacial stage due to the erosive power of glaciers as they advance (Dorr and Eschman, 1970). However, a weathered soil zone (the Sangamon paleosol) has been identified in boreholes in southern Michigan and northern Indiana (Kozlowski, 1999). The Sangamon paleosol serves as a hiatus marker bed between the two most recent glacial episodes (Kozlowski, 1999).

The surficial geology of the Nottawa Creek Watershed is a result of the last glacial stage (Wisconsinan) and was produced by glaciers between approximately 23,000 and 14,000 years ago (Moser and Passero, 1990; Kehew et al., 1999a). All of Michigan was covered by several thousand feet of ice during the glacial maximum of the Wisconsinan stage (Figure 3), as the continental ice sheet advanced as far south as southern Indiana (Leverett and Taylor, 1915; Dorr and Eschman, 1970). The orientation of the landforms within the Nottawa Creek Watershed indicate the ice in this area generally moved from northeast to southwest (Dorr and Eschman, 1970; Kozlowski, 1999). Previous studies have determined the surficial deposits and landscape were formed by the Saginaw ice lobe, a lobe of the massive continental Laurentide Ice Sheet (Leverett and Taylor, 1915; Moser and Passero, 1990).

The surficial deposits of the Nottawa Creek Watershed, collectively referred to as glacial drift, are complicated in nature, as they were formed or were deposited by advancing, retreating, and stagnant ice (Figure 4). The surface topography of the

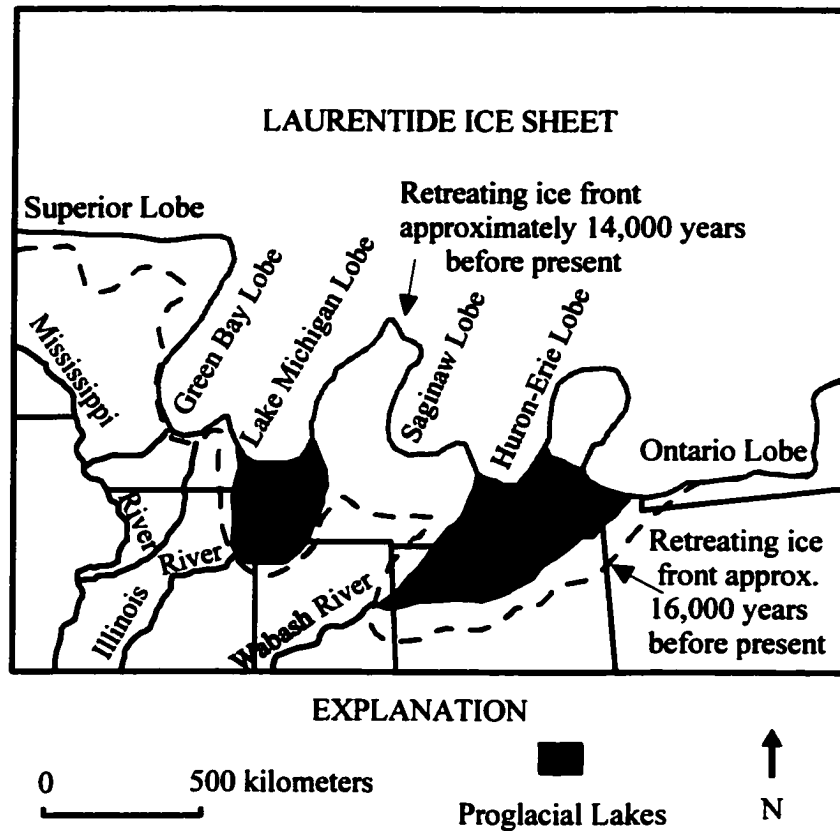


Figure 3. Generalized Schematic of the Great Lakes Region Glaciation (After WMU, 1992).

Nottawa Creek Watershed is largely characterized by flat areas or very gently rolling hills. The glacial landforms in the watershed include moraines, outwash plains and fans, and drumlins (Moser and Passero, 1990; Kozlowski, 1999; Kehew et al., 1999a). These landforms are typically underlain by till, outwash, or lacustrine silt and clay.

Till is deposited by a variety of processes that involve direct contact with glacial ice. It is a poorly sorted material composed of clay, silt, sand, gravel, and boulders. The Tekonsha moraine, a recessional or end moraine within the study area, is characterized by gently rolling arcuate hills composed primarily of sandy till

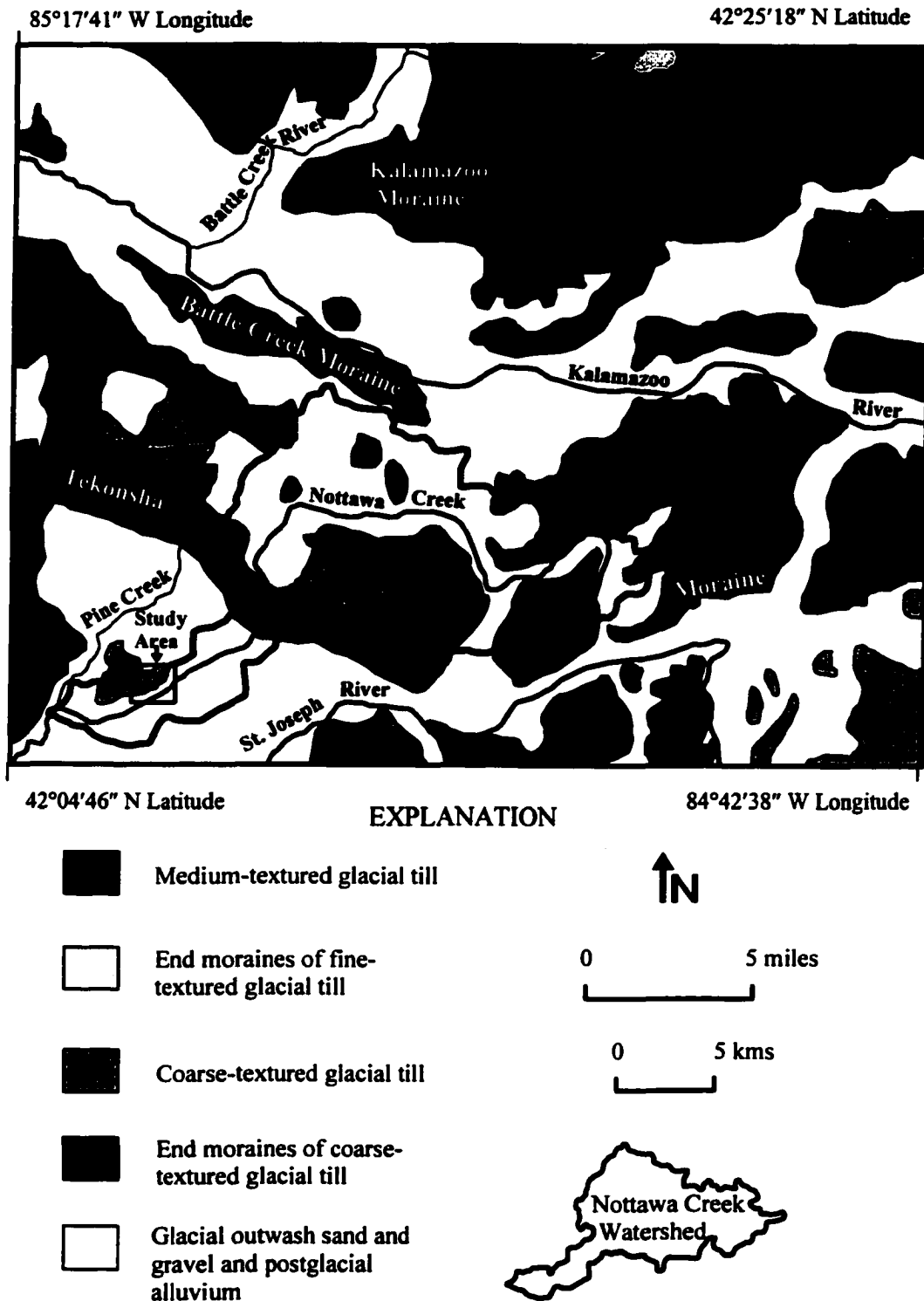


Figure 4. Generalized Glacial Geology of Calhoun County (After WMU, 1992).

(Moser and Passero, 1990; Kozlowski, 1999). The Tekonsha moraine formed as the glacier temporarily reached equilibrium; that is, it did not advance or retreat significantly although glacial ice continued to flow and deposit debris near its terminus. The moraine is dissected in places due to the erosive power of glacial meltwaters (Moser and Passero, 1990). Ground moraine, composed of till, was laid down as the glacier resumed retreating. Outwash deposits, deposited by melt-water streams, composed mostly of gravel and sand with very little silt and clay, filled portions of the major valleys and also occur on some plains or fans (Moser and Passero, 1990). The southern portion of the Nottawa Creek Watershed is characterized by streamlined subglacial landforms called drumlins, which trend southwest (Kehew et al., 1999a). The retreat of the glacier margin to the northeast was broken by a few short-lived readvances resulting in deposition of thin layers of till or outwash upon earlier deposits (Dorr and Eschman, 1970; Kehew et al., 1999b). The greatest thickness of drift in the Nottawa Creek Watershed, about 43 meters, is in the eastern section (Moser and Passero, 1990). The thinnest deposits, with a thickness of only 2 meters over shale bedrock, are along the valley of Nottawa Creek in the western section (Appendix A).

Modern cultural activities have since modified the landscape slightly. Most significant is the construction of drains, which have allowed extensive farming activities to exploit the rich soil that has developed over time. Post-glacial stream erosion and deposition is accentuated by these developments.

Bedrock Geology

The Precambrian basement of the Nottawa Creek Watershed is buried under approximately 2 km of Paleozoic sedimentary rock (Howell and van der Pluijm, 1990). The Paleozoic bedrock geologic history of the Nottawa Creek Watershed area is part of that of the Michigan Basin region (Dorr and Eschman, 1970; Moser and Passero, 1990). The Michigan Basin was occupied by shallow epeiric seas during a substantial portion of the Paleozoic Era (Dorr and Eschman, 1970). The most shallow bedrock formations of the Nottawa Creek Watershed only will be described here considering these are the sole formations tapped as a water supply.

In the western one third of the watershed, glacial sediments overlie Paleozoic age Coldwater Shale (Figure 5). The Marshall Sandstone covers the Coldwater Shale over most of the eastern two thirds of the watershed. The Antrim Sea covered the Nottawa Creek Watershed area about 350 million years ago (Moser and Passero, 1990). Layers of fine-grained muds and silts were deposited in the offshore marine environment (Dorr and Eschman, 1970; Moser and Passero, 1990). The Coldwater Shale Formation is the name given to the lithification of these Mississippian sediments (Dorr and Eschman, 1970; Moser and Passero, 1990). It is estimated that the Coldwater Shale ranges from approximately 150 to 300 meters in thickness throughout the watershed (Howell and van der Pluijm, 1990; Moser and Passero, 1990). The upper portion of the Coldwater Shale was likely subject to extensive weathering and fracture in the western portion of the watershed since several wells tap

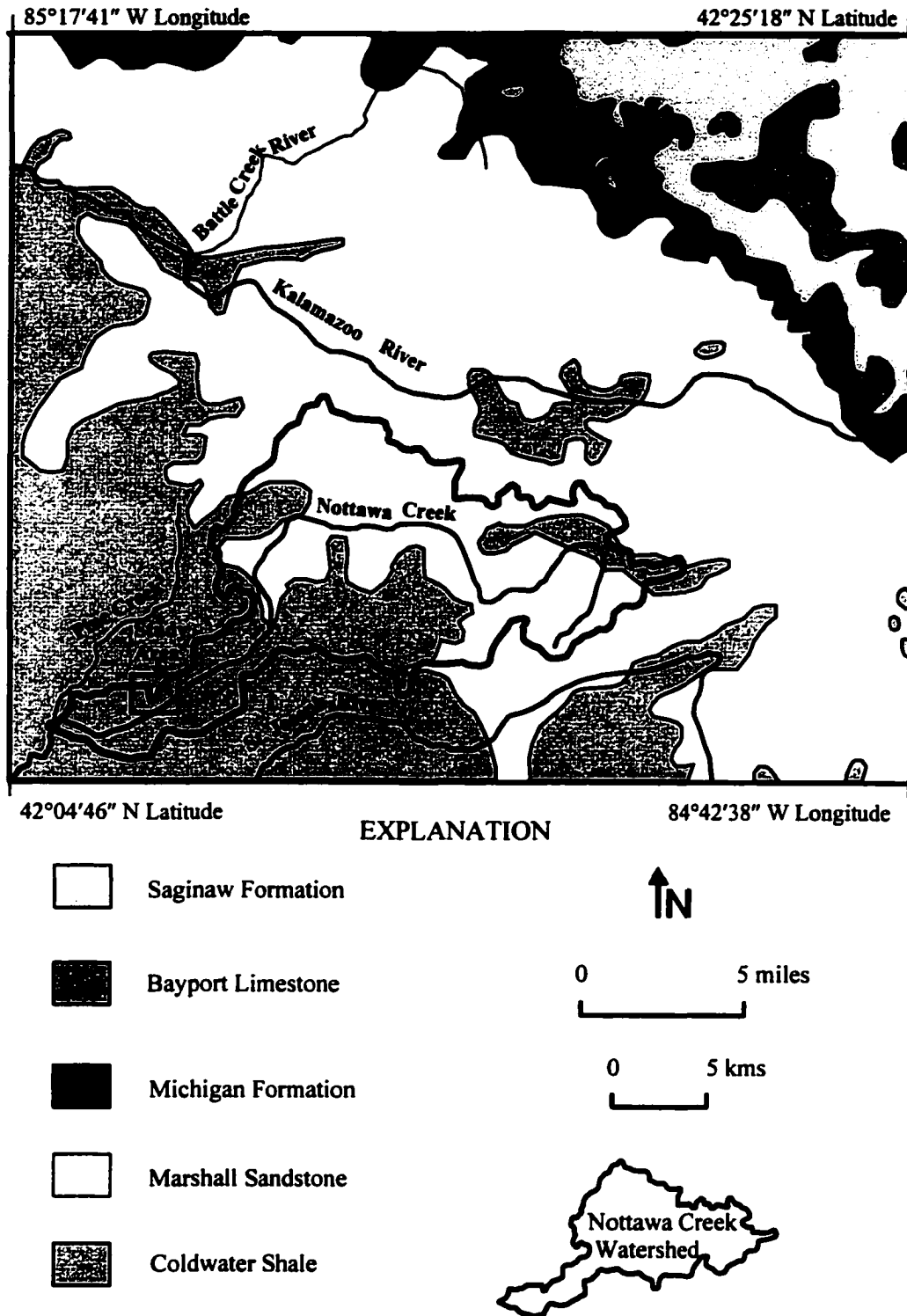


Figure 5. Generalized Bedrock Geology of Calhoun County (After WMU, 1992).

the shale as a water supply there (Moser and Passero, 1990).

Retreat of the Antrim Sea resulted in near-shore and beach environment deposits of silts and sands (Moser and Passero, 1990). These sediments later lithified into strata which became known as the Marshall Sandstone Formation (Moser and Passero, 1990). The Marshall Sandstone covers the Coldwater Shale conformably but is present only across the eastern 2/3 of the watershed (Harrel et al., 1991). The thickness of the Marshall Sandstone ranges from 0 to 60 meters over the course of the watershed (Moser and Passero, 1990). The Coldwater Shale and Marshall Sandstone dip gently toward the northeast in the direction of the center of the basin and strike northwest (Harrel et al., 1991; Moser and Passero, 1990; Dorr and Eschman, 1970). The uplift of the Michigan Basin and the subsequent erosion produced a varied bedrock surface with some bedrock valleys in Calhoun County approaching nearly 60 meters in depth (Moser and Passero, 1990).

Hydrogeology of the Nottawa Creek Watershed

Climate and Recharge Estimates

The study area is typified by a temperate climate. Monthly average temperature and precipitation for the years 1961-1990 as compiled by the National Weather Service station in Battle Creek are given in Table 1. Precipitation in the Nottawa Creek Watershed area averages 90.7 cm/yr, which include 132.6 cm/yr of

snow (~ 13 cm water equivalent). Air temperatures reach a high point in July with a monthly mean of 22.0°C and dip to a mean of -5.3°C in January.

Holtschlag (1997) gives a generalized normal estimate of recharge for the Nottawa Creek drainage basin of 27.4 cm/yr. The remainder (63.3 cm) of yearly precipitation occurs as runoff or is recycled to the atmosphere as evapotranspiration.

Table 1

Monthly Average Temperature (°C), Precipitation (cm), and Snow (cm) for 1961-1990 Summary

	Ja	Fe	Ma	Ap	Ma	Jn	Jl	Au	Se	Oc	No	De
T	-5.3	-4.0	1.9	8.6	14.6	19.7	22.0	20.9	16.9	10.5	4.3	-2.5
P	4.09	3.94	6.76	8.69	9.07	9.04	8.71	9.02	9.63	7.01	7.67	7.06
S	33.0	26.4	17.3	7.4	0.0	0.0	0.0	0.0	0.0	0.8	14.0	33.8

The recharge rate was developed by a hydrograph separation technique in conjunction with analysis of a 24 year record of streamflow and precipitation along with basin-characteristics data (Holtschlag, 1997). The USGS streamflow-gaging station is approximately 4 miles southwest of Athens, which recorded a daily streamflow value from 10-1-1966 to 9-30-97 (Blumer et al., 1998). The average daily streamflow for 31 years is 4.3 meter³/second. The gaging station was taken out of service in 1997 (Blumer et al., 1998).

Hydrogeology

The glacial sediments, which may serve as an aquifer, vary from 2-43 meters in thickness and overlie Paleozoic age Coldwater Shale in the western one third of the watershed. The Coldwater Shale serves as an aquifer in a limited capacity when fractured. The Coldwater Shale is covered by the Marshall Sandstone in the eastern two thirds of the watershed. The Marshall Sandstone serves as a prolific source of water where present (Moser and Passero, 1990).

A farm near the mouth of the watershed (see Figure 2) has been chosen as a model for the Nottawa Creek Watershed Project because this area seems particularly sensitive to possible agricultural contamination of the aquifers. The western 1/3 of the watershed is especially vulnerable because of the thin glacial drift cover (average ~ 12 m) overlying the Coldwater Shale. The Village of Athens was fortunate in that the 15 m deep shallow NO_3^- contaminated well could be discontinued in favor of potable, but more mineralized, groundwater drawn from two 39 m deep wells screened in glacial drift. A possible buried bedrock valley begins at Athens and may trend to the south as indicated by some deep irrigation wells (Kozlowski, 1999). Although relocation of Athens's water supply well is a partial solution, it is costly for the village as the water must be treated for iron and manganese.

Heath (1983) cites a range of hydraulic conductivity estimates for glacial till of 10^{-7} to 0.3 m/d and an estimate of 0.05 to 300 m/d for silty to clean sands. Hydraulic conductivity estimates for the Marshall Sandstone are reported in

Grannemann and Twenter (1985) as 45 m/d for the upper sandstone aquifer and 168 m/d for the lower sandstone aquifer. Grannemann and Twenter (1985), in their study of the Verona well field, Battle Creek, define the upper sandstone as approximately 23 m thick and separated from the 12 m average thickness lower sandstone aquifer by a 3 m thick siltstone bed.

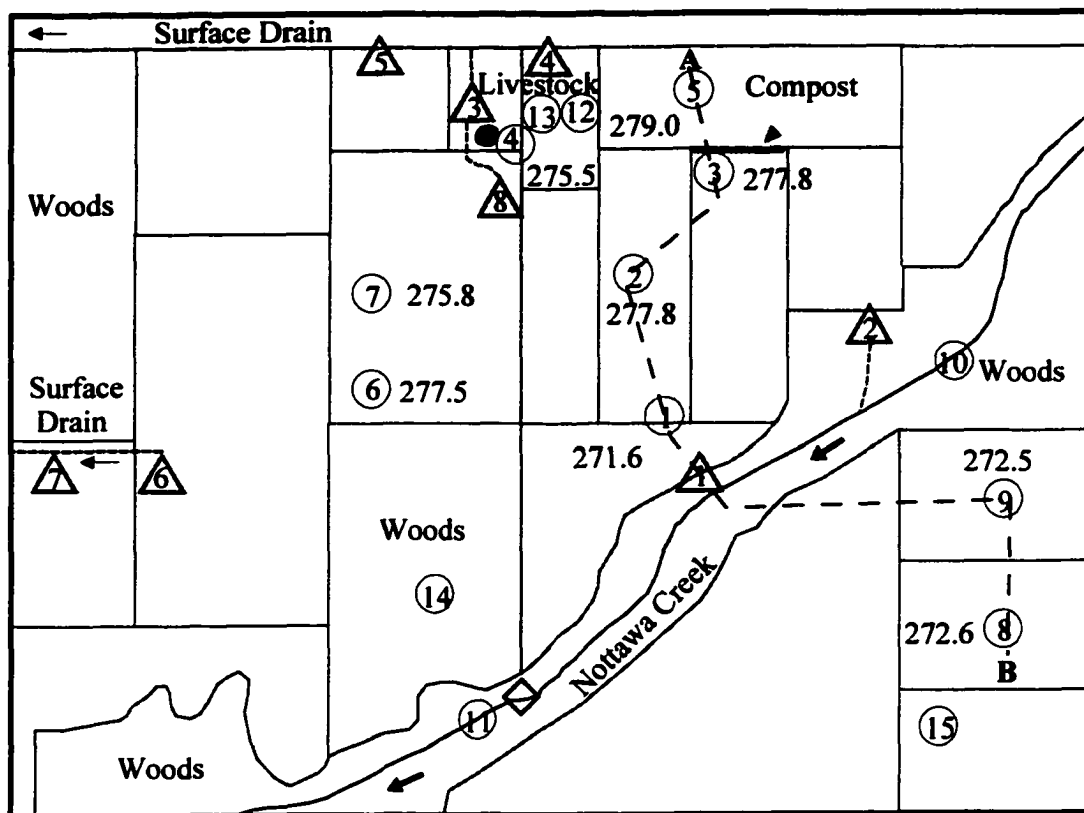
CHAPTER III

METHODOLOGY

Study Area Description

The research was conducted on a private working farm and surrounding area that may serve as a "model" for similar farms and agricultural areas throughout the Nottawa Creek Watershed. The study region covers an area of approximately 4 km² (Figure 6). During the Fall of 1999, an observation well network of 9 shallow water table wells (MW-1 through MW-9) was installed within an agriculturally intensive area near the mouth of the Nottawa Creek Watershed. This work was completed utilizing the WMU Department of Geosciences drill rig. Two streambed wells (MW-10 and MW-11) were installed May of 2000 and provide water quality data of groundwater discharging into the stream. The stream (Nottawa Creek) was also sampled for surface water quality. Four domestic drift wells (MW-12 through MW-15) and eight tile-drains (TD-1 through TD-8) were also included in the sampling plan.

The observation well elevation survey was performed utilizing a Sokkisha® infrared unit and total station survey. Static water level elevations from June 2000 are shown in Figure 6. A hydrogeologic section is shown in Figure 7.



EXPLANATION

0 610 meters



● Lagoon

△ Tile drain outlet

◇ Stream sampling site

① Monitoring well

A - - B Trace of hydrogeologic section (section shown in Fig. 7)

Figure 6. Static Water Levels for June 2000 (Elevation in m).

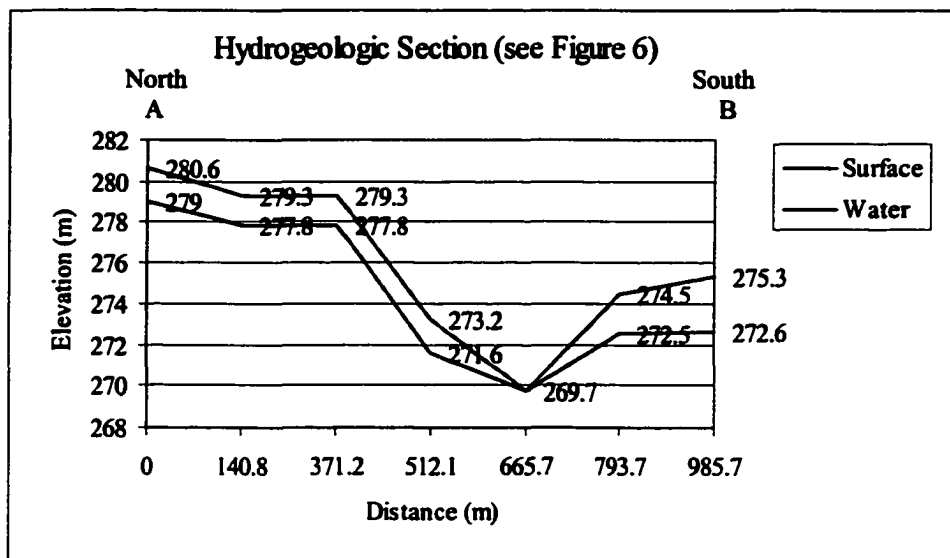
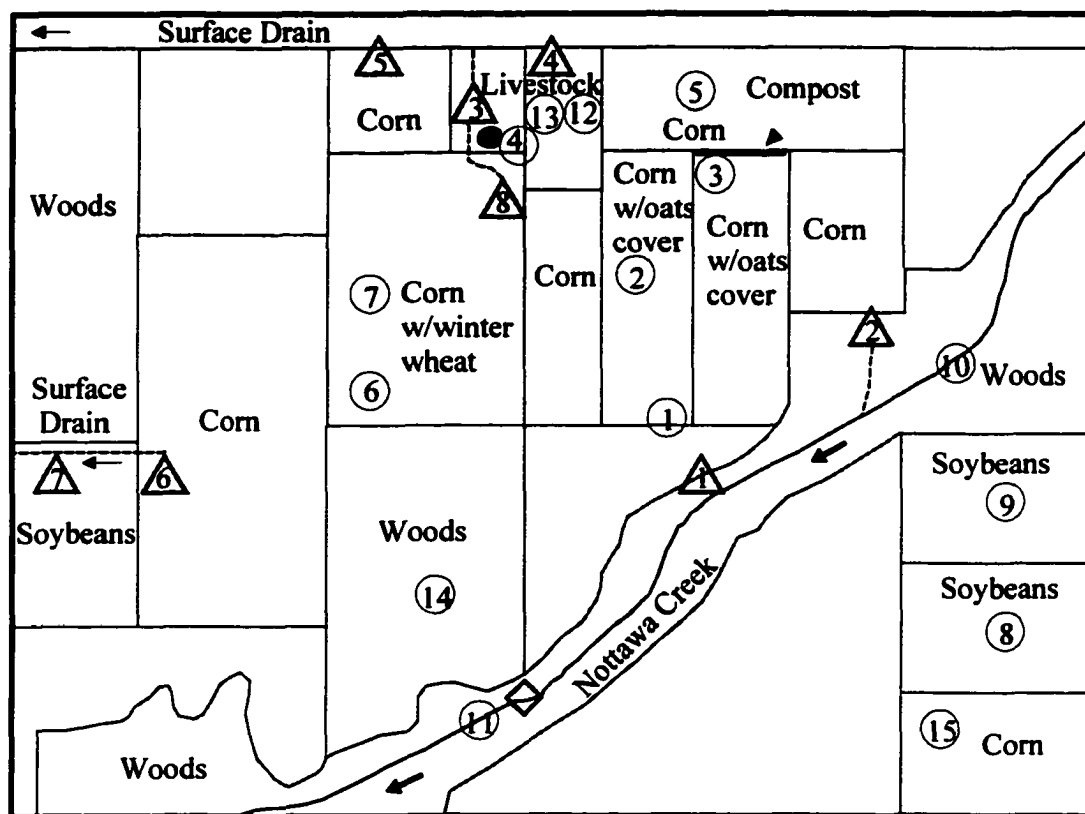


Figure 7. Hydrogeologic Section Depicting Ground Elevation and Static Water Level Elevation from June 2000.

The livestock operations are concentrated in a designated area (see Figure 6). On the average, 300-1000 swine are kept as a confined feeding operation in outbuildings or field sites. The animal waste sewage lagoon has been in place since at least 1972. The farm also has approximately forty-five 136+ kg cows, which are kept in pasture. In late 1999, approximately 100 calves were purchased as starter beef calves. The 3-5 day old calves were initially fed milk and then weaned to grain. The calves were sold at auction upon attaining a weight of approximately 113 kg. This endeavor was subsequently discontinued.

Crop rotation records were recorded for 1999, 2000, and 2001 (Figures 8-10) to note changes in groundwater chemistry with changes in agricultural practices. Corn and soybeans are the major crops grown with some hay and occasional winter wheat. Corn requires fertilization while soybeans do not. Composted manure is spread and



EXPLANATION

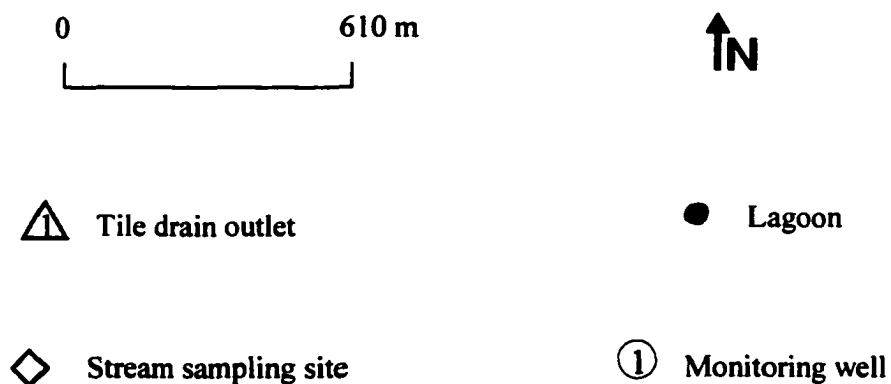
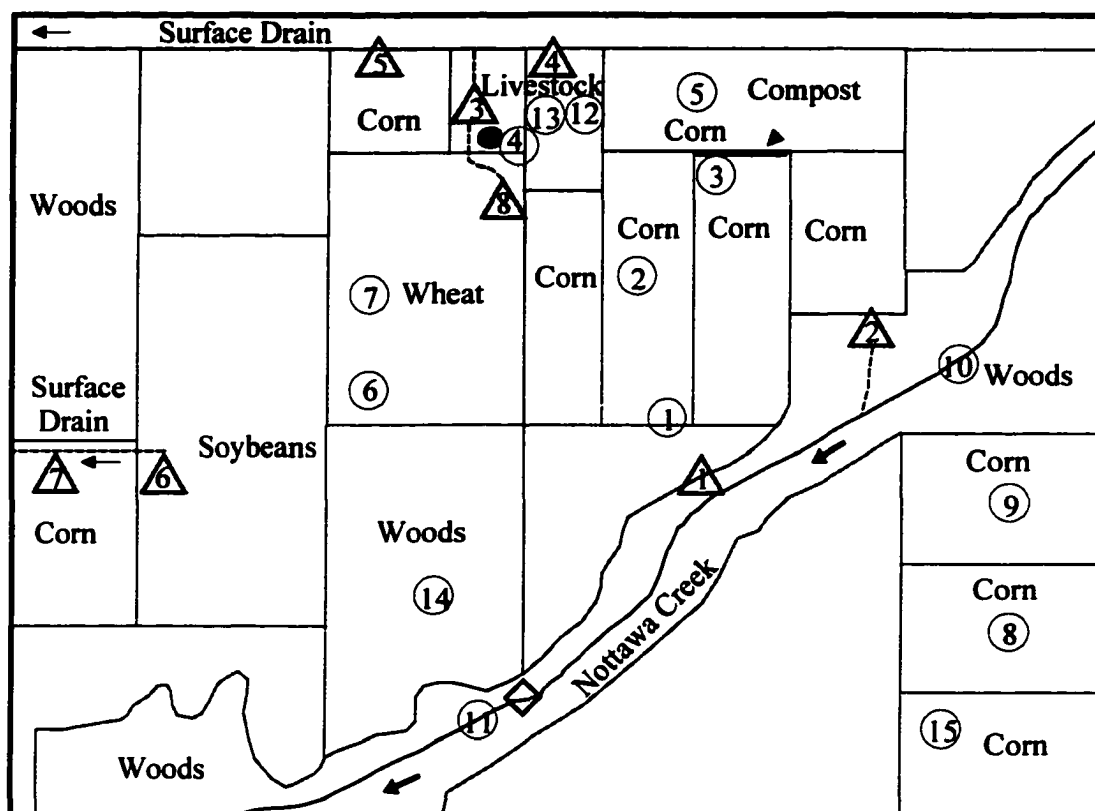


Figure 8. Schematic of Study Area with Crops Grown During the Year 1999.



EXPLANATION

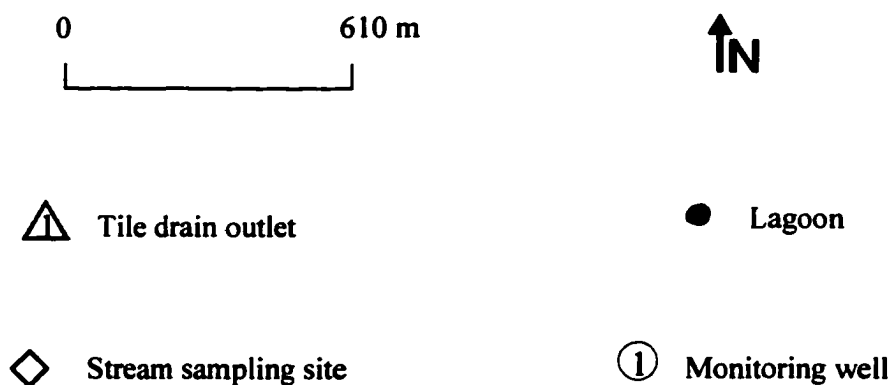
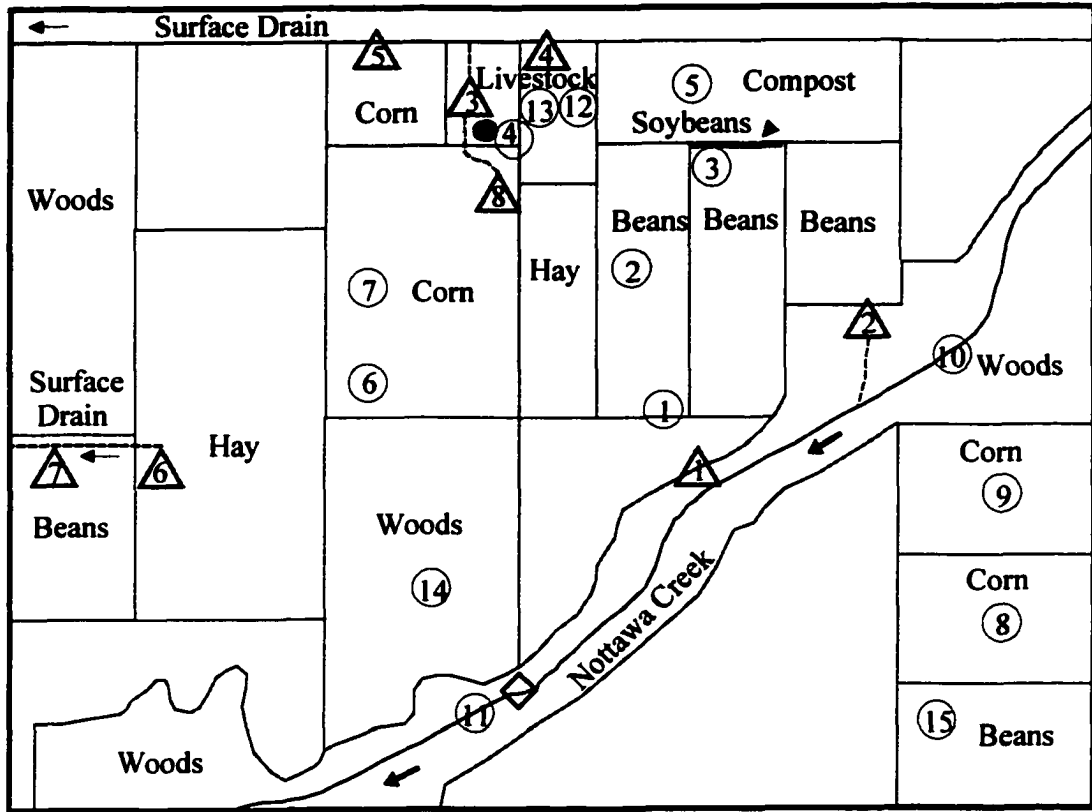


Figure 9. Schematic of Study Area with Crops Grown During the Year 2000.



EXPLANATION

0 610 m



△ Tile drain outlet

● Lagoon

◇ Stream sampling site

① Monitoring well

Figure 10. Schematic of Study Area with Crops Grown During the Year 2001.

chisel plowed in early spring, or preferably 10-15 days before planting at a rate of 5.7-7.6 m³/acre. Liquid manure is pumped from the lagoon and spread at a rate of 30.2-34.1 m³/acre. A fertilizer analysis from the University of Wisconsin Soil and Forage Analysis Laboratory (Marshfield, WI) reported the combined compost and liquid manure available N content at approximately 22.7 kg/acre at the rate applied. In 1999 and 2000, synthetic fertilizer in the form of 28% N was applied to corn fields to make up the nitrogen deficiency. In 2001, dry urea was applied at the rate of 45.4 kg of N per acre and disked into the soil to make up the nitrogen deficiency for corn growth. Occasionally, a conservation method is employed whereby an oats cover crop is planted in the fall on corn stubble in order to store nutrients. Then, the oats are plowed under in the spring and corn is typically planted. Wheat, when seeded, is planted in the fall until a mid-July harvest. Manure is then spread at the rate of 30.2-34.1 m³/acre, and the field planted in an oats cover crop. The farm recycles virtually all materials. For example, the wheat stems are collected and used as livestock bedding and then added to the compost pile.

A soil analysis report (not shown) from 1997 has also been furnished. In general, the goal is to attain the projected desired level of minerals and nutrients for a given field. In 1999, a private firm mixed the fertilizer and spread it for \$4./acre. It is also considered beneficial to strive for a Ca:Mg ratio of 7:1. This is achieved by applying 500-1000 lbs/acre of Belleview Lime if needed. The variation in loading is estimated by distinguishing levels of OM (organic matter) and CEE (cation exchange capacity). The higher OM and CEE, the more lime the soil can hold.

Test Drilling

Monitoring wells were installed utilizing Western Michigan University drilling equipment and personnel. The hollow-stem auger drilling method was most frequently employed. The 2 streambed wells were manually driven. The 2 wells directly beneath the stream (see Figure 10) consisted of 0.9-meter stainless steel, 10-slot screens driven into the streambed. These wells were driven approximately 0.3 to 0.6 meters below the streambed. Galvanized casing served as the well extension. Water temperature and DO (dissolved oxygen) concentrations were measured to ensure water sampled from the streambed wells was groundwater. Stream parameters ranged from 14.2-14.5 °C for temperature and 8.2-8.5 mg/L for DO. Groundwater measurements ranged from 11.4-13.1 °C for temperature and 0.3-0.5 mg/L for DO.

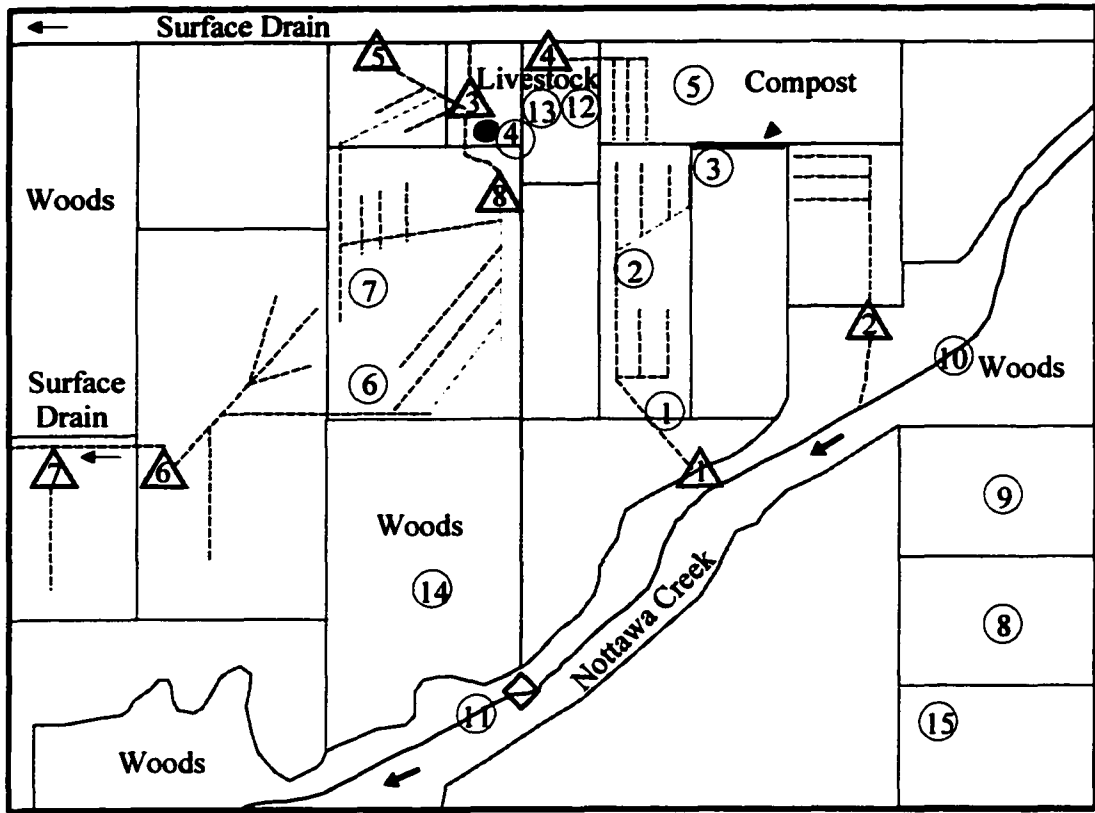
Five centimeter outside diameter PVC (polyvinyl chloride) casing was installed through the annulus of the auger for the hollow-stem auger method, making use of either 1.5 or 3.0 meter, 10-slot screens. Monitoring well 5 was an exception with the utilization of five centimeter galvanized casing and a 1.8-meter stainless steel, 10-slot screen. The natural collapse method was most commonly employed due to the 8.26 centimeter inside diameter of the auger. It was possible to place a sand pack from 0.6 meters below to 0.6 meters above the screened interval for fine-grained sediments. A 0.6 meter bentonite seal was placed above the sand pack or natural formation material. Natural material was then used to complete the backfill and construct a mound around the casing at the surface to divert surface runoff.

All installed monitoring wells were equipped with a locking protective cap. Other monitoring wells shown in Figure 6 (MW-12 to MW-15) are domestic wells which are sampled from a tap.

Field records were documented and cuttings collected during drilling (see Appendix A), which assists in scrutinizing the effects of hydrogeology on nutrient and herbicide movement dynamics. The soils in the study area can generally be classified as silty to sandy loam.

The monitoring well network and tile drain configurations are shown in Figure 11. Silty to medium-textured sandy loams are drained by black plastic tile 46 centimeters to 1.8 meters deep. The tiles vary from 50 to 12 meters apart depending on whether the soil is silty or medium-textured sandy loam. Coarse textured sandy loam soils ordinarily do not require subsurface drains. For example, the medium to coarse textured soils on the south side of Nottawa Creek within the study area are well drained.

Depth to water levels for monitoring wells varied from 1.8 to 3.8 meters for low flow conditions of December 1999 (Appendix A). All water level measurements were made by the investigator utilizing a single Herron® Instruments water level indicator. Water levels and altitude indicate groundwater is generally flowing toward Nottawa Creek. However, a groundwater divide appears to exist between MW-6 and MW-7. Water levels measured during groundwater high flow conditions also suggest a groundwater divide in this area with MW-7 groundwater flowing north in the direction of a surface drain.



EXPLANATION



0 610 m

— Tiles

△ Tile drain outlet

● Lagoon

◇ Stream sampling site

① Monitoring well

Figure 11. Tile Drain Schematic for Subsurface Drainage.

Water Quality Sampling Overview

The monitoring plan for each of the wells, drains, and surface water sites was, in general, to sample from December 1999 to September 2001. Due to time constraints, the September 2001 geochemical data were not discussed in the dissertation, although test results are included (see Appendix B for chemical parameter values). The goal of the sampling program was to sample each source quarterly, for all parameters with an additional May and July monthly sampling for herbicides, ammonia, nitrate + nitrite, total phosphorus, and total organic carbon. The sampling program, over essentially a two year period, afforded repeated seasonal testing. The sampling calendar is illustrated in Table 2.

Table 2
Project Sampling Calendar

1999	2000	2001
	March 12, 19, 2000	March 11, 18, 2001
	May 13, 14, 2000	May 12, 13, 2001
	June 11, 18, 2000	June 9, 10, 2001
	July 15, 16, 2000	July 7, 8, 2001
	Sep. 24, Oct. 1, 2000	Sep. 8, 9, 2001
December 12, 1999	December 10, 26, 2000	

Repetition of seasonal sampling events can provide information on hydraulic connections between surface water and groundwater. For example, the March sampling date is an ideal time to catch the spring flushing of nitrate from the winter thaw. The May event coincides with a spring compost/sludge application along with a pre-emergent herbicide. The July sampling event was included to possibly detect early summer synthetic fertilizer and herbicide application. In general, the need for repeated sampling events can be realized by noting the variations in concentrations of analyses (Appendix B). However, it should be noted nitrate values may not truly represent the minimum and maximum concentrations over the course of the study. Muldoon and Madison (2000), in their study of a shallow, sandy aquifer, utilizing an automated observation well nitrate monitoring system, suggested groundwater recharge events and crop uptake control variations in nitrate concentrations. Consequently, periodic sampling events only can miss detection of peak concentrations which may occur during the course of a study.

Quarterly sampling typically occurred on a given Sunday and the drains either the previous or following Sunday, depending on weather, and delivered to the lab on Monday. Intermediate sampling events occurred on a Saturday and Sunday and were delivered to the lab on Monday. The MDEQ laboratory required a one week advance notice, which somewhat restricted the timings of the sampling events. The first round of sampling took place December 12, 1999. The drains were not flowing because of the unusually dry weather.

There are 15 monitoring wells, 8 tile drains, and 1 surface water site in the

investigation. The parameters to be sampled are listed in Table 3. The metals were field filtered utilizing a 0.45 μm high-capacity Quickfilter™ (QED Environmental Systems, Inc., Ann Arbor, MI).

Table 3
Chemical and Isotopic Parameter List

General	Nutrients	Metals	Anions	Isotopes	Herbicides*
TOC	$\text{NO}_3^- + \text{NO}_2^- - \text{N}$	Ca^{2+}	Cl^-	$^2\text{H}/^1\text{H}$ of H_2O	Atrazine
TDS	$\text{NH}_3 - \text{N}$	Mg^{2+}	SO_4^{2-}	$^{18}\text{O}/^{16}\text{O}$ of H_2O	Alachlor
Alkalinity	Total P	Na^+	HCO_3^-	$^{13}\text{C}/^{12}\text{C}$ of H_2O	2, 4-D
	o-Phos	K^+	CO_3^{2-}	$^{15}\text{N}/^{14}\text{N}$ of NO_3^-	
		Fe^{+2}		$^{18}\text{O}/^{16}\text{O}$ of NO_3^-	
				^3H of H_2O	

*Immunoassay testing with selected samples analyzed by USEPA approved methods.

Nitrate is reported by the lab as nitrate plus nitrite. Nitrite occurs as an intermediate oxidation state of nitrogen and is assumed not to be present in concentrations large enough to influence ionic balance to a noticeable degree (Manahan, 1993; Hem, 1985). For example, based on a previous study within the watershed, the largest concentration of nitrite reported was 0.004 mg/L as nitrite-nitrogen (Kehew et al., 1999a). Testing for nitrite for this study was performed on a one-time basis for the June 2000 sampling event. The largest concentration of nitrite

reported was 0.08 mg/L and represents less than 0.7% of the total nitrate + nitrite levels measured. Based on the above discussion and reported results, nitrate + nitrite as nitrogen will be referred to as nitrate as nitrogen for the remainder of the text.

Field measurements for this study included pH, DO, T (temperature), and SC (specific conductance). pH, T, and SC were measured with an Orion Model 341450 pH/T/SC meter. DO and T were measured with a YSI Model 95 DO/T meter. The DO meter became available beginning with the May 2000 sampling event.

Sterile plastic 500 ml sample bottles were provided by the MDEQ, whose environmental quality lab performed all chemical analysis except for herbicides and isotopes. Guidelines for preservation of samples were provided by the MDEQ. Herbicides were analyzed by the Michigan Department of Agriculture (MDA) with immunoassay tests. Utilizing USEPA approved methods, the MDA, KAR Laboratories, Inc. (Kalamazoo, MI), and USGS Organic Geochemistry Research Laboratory (Lawrence, KS), analyzed selected samples for various corn and soybean herbicides and degradation products. Stable isotopes of NO_3^- were analyzed by the University of Waterloo Environmental Isotope Laboratory, Canada as were stable isotopes of H, O, and C collected in June 2001. The WMU Stable Isotope Laboratory analyzed water samples collected in September 2001 for stable isotopes of O and C. Guidelines for collection of herbicides and stable isotopes are discussed in subsequent sections.

Two DC pumps were employed for collection of samples; a Whale® (Whale Water Systems, Peabody, MA) submersible pump and a Geopump2® (Geotech,

Denver, CO) peristaltic pump. In general, low permeability wells were purged the day before sampling. At least 3 bore volumes were purged from other wells before collecting a sample. Samples were collected from domestic wells at a tap, allowing water to run for at least 5 minutes to clear the line. The stream samples were collected mid-stream via a pump. Tile drain specimens were gathered by way of grab samples. Metals were field filtered, where possible, by placing a five gallon bucket beneath the tile drain outlet and subsequently obtaining the sample through pumping.

The QA/QC (quality assurance/quality control) program was designed to keep costs at a minimum. Generally, two duplicate samples were obtained per sampling event. Decontamination procedures involve emptying residual water in the pumping hose by gravity. In addition, distilled water was used to rinse off equipment to avoid cross contamination. These methods seem to be suitable for this situation. For example, MW-7 (one of the least contaminated wells) was sampled directly after MW-4 (the most highly contaminated well) during the July sampling event. Concentration values of NO_3^- -N were 140 mg/L for MW-4 and 0.04 mg/L for MW-7.

Comparison of Field Scale Model Monthly Infiltration Rates to Estimated Basin Recharge

Groundwater recharge assessment is inherently difficult due to many complexities (Holtschlag,1997). Soil lysimeters completed below the rooting zone provide the only direct measurement (Holtschlag,1997; Stephens, 1996). However,

even this appraisal is likely subject to some uncertainty due to disturbed soil (Stephens, 1996). In addition, the evaluation is typically complicated by short term measurements over time which may or may not be representative of long term climatic conditions (Stephens, 1996). Moreover, results of field scale infiltration studies at the catchment scale can lead to misleading results because of lateral variations in pedons and preferential flow routes (Kutilek and Nielsen, 1994). Because long term lysimeter data are in fact rare, recharge rates are commonly estimated by other methods (Holtschlag, 1997).

Determining temporal variation and specific amounts of recharge becomes particularly important in agricultural areas because of potential leaching of pesticides and nutrients. The numerical water-balance model GLEAMS (Groundwater Loading Effects of Agricultural Management Systems; Leonard et al., 1987), modified from its predecessor CREAMS (Chemical, Runoff, and Erosion from Agricultural Management Systems; Knisel, 1980), is a predictive tool to analyze effects of different cropping management systems on water resources. The computer model GLEAMS is in the public domain and accessible from the Internet (Knisel et al., 1994). Input parameters include crop history, climatic data, soil layers and accompanying physical characteristics. The water balance computations solve for plant water uptake requirements, evaporation, and runoff. The remainder of water not held in storage becomes available for deep percolation or recharge.

Local recharge rates within basins can differ considerably from basinwide averages because of local variations in basin infiltration capacities (Holtschlag, 1997).

The objective of this research is to quantify the average field scale amount in monthly increments of recharge.

This research may serve as a model for the Nottawa Creek basin in that 2 distinct soil units representative of the basin were modeled; that is, soils which require tile drains and well drained soils. The USDA (1992) classifications are, respectively, a well-drained sandy loam (Oshtemo) and a somewhat poorly drained sandy loam (Brady).

The computer model GLEAMS was utilized for calculating deep percolation or recharge. A study by Holtschlag (1997) of groundwater recharge for the basin served as the comparison model.

Climatic data were available from two real-time remote weather stations near the study site (see <<http://www.agweather.geo.msu.edu>>). The Athens station is approximately 2 miles southwest of the study area while the Ceresco station is approximately 6 miles northeast of the study area. The weather information is relayed by telephone and posted on the Internet daily and monthly.

A BASIC Triangular Finite Element Groundwater Flow Model

A groundwater flow model was developed to aid in understanding of the regional and local flow system. Conceptually it appeared there may be a groundwater divide in the study area with groundwater flow both toward Pine Creek and Nottawa Creek (Figure 12).

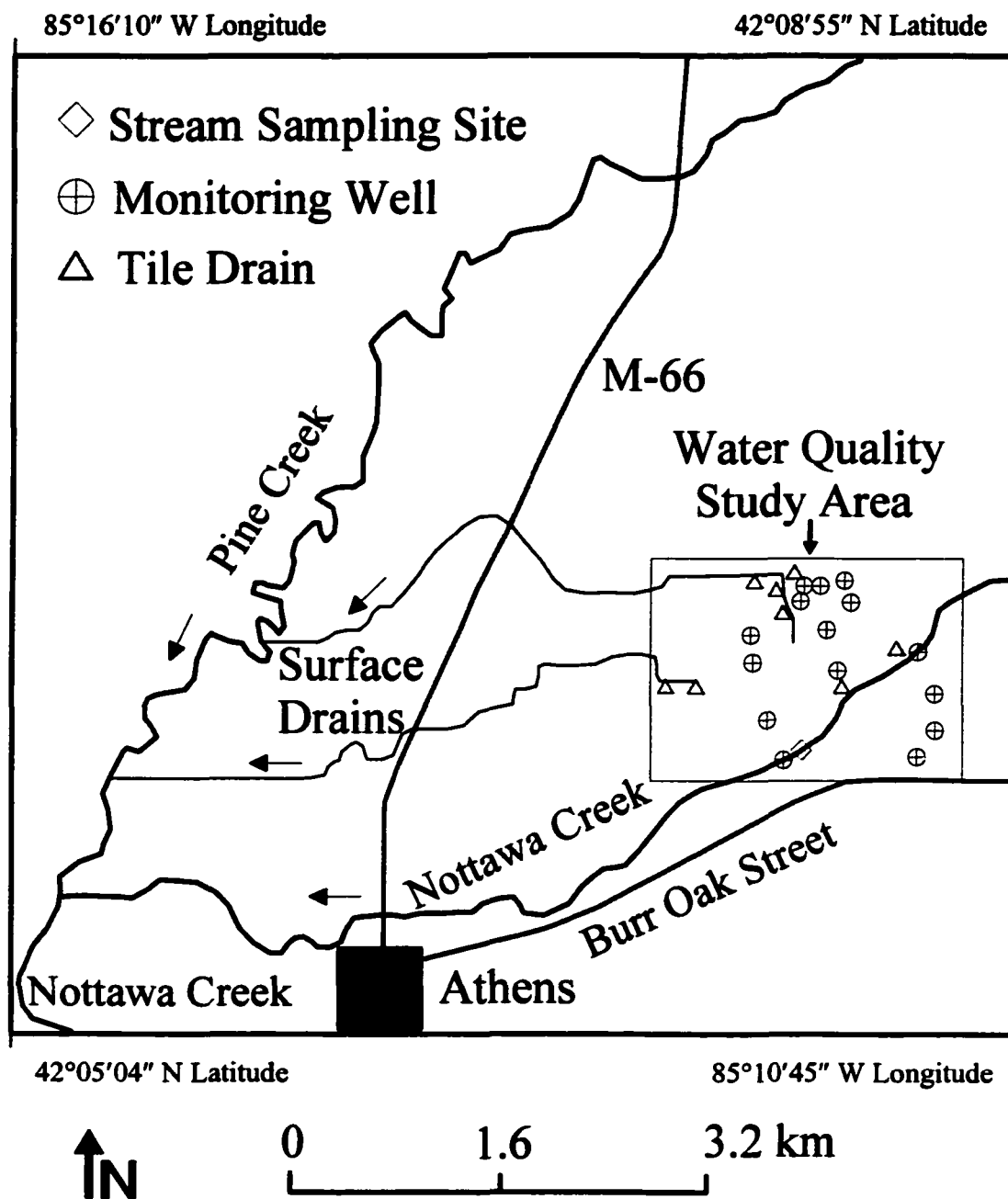


Figure 12. Study Area for the Regional Groundwater Flow Model.

The partial differential equation for groundwater flow cannot be solved directly and is replaced by a set of algebraic equations (Bear and Verruijt, 1987). A computer code, using a digital computer, is utilized because of the very large number of equations that have to be solved simultaneously. The computer program developed to solve the groundwater flow equation in this study is a modification of an original code by Kinzelbach (1986) and is documented in Unterreiner (1997). Recoding of the program by Kinzelbach (1986) consisted of conversion from an older version of BASIC (Beginner's All-purpose Symbolic Instruction Code) to Microsoft Corporation's 4.5 version of QBASIC (QuickBASIC). BASIC is an excellent language for computer programming because it is powerful, flexible, and utilizes English-like code that is easy to use (Halvorson and Rygmyr, 1991). Other modifications to the code by Kinzelbach (1986) included reformatting data input and output files as well as creating files for graphics packages (Unterreiner, 1997).

The computer program calculates hydraulic head for a two-dimensional one-layer confined aquifer by the Gauss-Seidel iterative method (Kinzelbach, 1986). The groundwater flow model for this study involves an unconfined aquifer. The code by Kinzelbach (1986) may be applied to an unconfined aquifer simulation assuming changes in saturated thickness are small compared to the overall thickness, the hydraulic gradient is equal to the slope of the water table, and flow is horizontal (Anderson and Woessner, 1992; Wang and Anderson, 1982). The program is also limited to solving the continuity equation for steady state flow (Kinzelbach, 1986).

The numerical methods require that the area of interest be subdivided by a

grid into a number of smaller subareas. The model is divided into subareas, called elements. Triangular elements were chosen as subareas for this study with each of the three corners defining a node where the hydraulic head will be determined. Figure 13 illustrates how the nodes and elements are numbered.

The computer code consists of a matrix in which the matrix coefficients are calculated from the coordinates of the nodes along with the transmissivity. A subroutine solves the system of linear equations by interpolation where the solution will be in terms of the hydraulic head at every node (Kinzelbach, 1986).

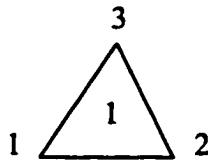


Figure 13. A Simple Example Shows How the Nodes and Elements Are Numbered.

Spatial and Temporal Geochemistry Trends in Groundwater, Agricultural Drains, and Surface Water

Funding for this research was provided through the USEPA under Section 319 of the Clean Water Act and administered by the MDEQ through WMU's GEM Regional Center. All samples were analyzed by the MDEQ Environmental Quality Laboratory utilizing appropriate USEPA laboratory methods.

Water samples were collected for chemical analyses of major ions, TOC, ortho-P, Total P, TDS, NH_3 , and NO_3^- -N quarterly (December, March, June, and

September) for selected residential wells, observation wells, tile drains, and surface water (Table 4). Two monthly sampling events in May and July, in addition to quarterly testing, served to analyze solely for TOC, NH_3 , NO_3^- -N, and Total P. Total phosphorus includes phosphates, as well as all other phosphorus forms. Total ammonia as reported by the MDEQ laboratory, includes ammonium ion and unionized ammonia as nitrogen. Field measurements included pH, dissolved oxygen, temperature, and conductivity.

Table 4

Geochemical Parameter List

General	Nutrients	Metals	Anions	Field Measurements
TOC	NO_3^- -N	Ca^{2+}	Cl^-	pH
TDS	NH_3 -N	Mg^{2+}	SO_4^{2-}	Conductivity (SC)
Alkalinity	Tot P	Na^+	HCO_3^-	Temperature (T)
	o-Phos	K^+	CO_3^{2-}	Dissolved Oxygen (DO)
		Fe^{+2}		

Evaluating Shallow Groundwater Vulnerability with Environmental Isotopes

This portion of the research utilizes stable isotopes of H, O, and C, and tritium, a radioactive isotope of hydrogen to evaluate shallow groundwater

susceptibility to contamination. H, O, and C stable isotopes are considered environmental isotopes due to their abundance in our surroundings (Clark and Fritz, 1997). Stable isotopes of H, O, and C do not decay but rather fractionate due to physical and chemical processes (Clark and Fritz, 1997). Stable isotopes are measured as the ratio of the two most abundant isotopes of a given element.

Cane and Clark (1999), Kehew et al. (1998), and Hendry et al. (1983), have shown how use of O and H environmental isotopes can be applied toward increased understanding of groundwater flow and recharge processes. The stable isotope of H with the greatest mass is commonly referred to as D (deuterium). Clark and Fritz (1997) described how the difference in isotopic ratios ($^{18}\text{O}/^{16}\text{O}$ and D/H) of stream water between base flow conditions and periods of storm runoff can be used to separate the contribution of ground water discharge to the stream from surface runoff due to evaporation of lighter isotopes.

Atekwana and Krishnamurthy (1998) and Nascimento et al. (1997) have demonstrated how environmental isotopes can be used to improve knowledge of carbon cycling, which is a vital component in nitrate movement dynamics. For example, the carbon for denitrification originates from an organic source which is isotopically more ^{13}C depleted compared to that of the DIC alkalinity pool (Atekwana and Krishnamurthy, 1998; Nascimento et al., 1997).

The isotopic composition of O, H, and C, determined by mass spectrometry, is expressed in per mil (parts per thousand) ‰ deviations from a standard. δ notation is defined as

$$\delta \text{‰} = (R_{\text{Sample}}/R_{\text{Standard}} - 1) \times 10^3$$

where $R = \text{D/H}$, $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$ of the sample and standard respectively.

The IAEA (International Atomic Energy Agency) reference for D and ^{18}O in water is VSMOW (Vienna Standard Mean Ocean Water) while VPDB (calibrated using a fossil belemnite from the Cretaceous Pee Dee Formation in South Carolina) is the standard for ^{13}C of DIC (Kehew, 2001).

Samples for stable isotope analyses of hydrogen and oxygen of water, and carbon of dissolved inorganic carbon (DIC) were collected in June and September 2001. O and H samples were collected in 20 ml scintillation vials. June 2001 DIC samples were collected in 1 liter plastic bottles with no preservatives and were promptly refrigerated. All samples were filled to the top with no head space and air tight to prevent evaporation. September 2001 DIC samples were collected following a procedure developed by Atekwana and Krishnamurthy (1998). Water samples (10 ml) were injected into evacuated septum tubes pre-loaded with phosphoric acid and a magnetic stir bar.

Tritium (T or ^3H) is an environmental radioactive isotope of hydrogen with a half-life of 12.43 years (Clark and Fritz, 1997). Natural tritium is formed in the upper atmosphere and produced by neutron bombardment of nitrogen by the reaction (Clark and Fritz, 1997)



and forms water as T reacts with O (Kehew, 2001)



T is measured in tritium units (TU) where 1 TU = 1 ^3H per 10^{18} hydrogen atoms (Clark and Fritz, 1997). T serves as a marker for groundwater age dating since a huge tritium peak was generated in 1962-63 by thermonuclear bomb tests (Clark and Fritz, 1997). A qualitative interpretation for groundwater recharge is 5-15 TU for modern or post-bomb water (<5 to 10 yr) with less TU signifying submodern and greater representing some "bomb" T present (Clark and Fritz, 1997).

Tritium samples were collected from the two streambed wells in Oct., 2000 for T analysis by the University of Waterloo Environmental Isotope Laboratory (EIL). One liter of water per well was collected in (2) 500 ml plastic bottles for enriched analysis and filled to the top with no head space and air tight to prevent evaporation.

Liquid scintillation counting (LSC) is the technique used by the EIL for the detection and quantification of tritium. Samples are enriched approximately 15 times by electrolysis and then counted. The detection limit for enriched samples is 0.6 +/- 0.8 TU.

Tracing Nitrogen Sources with Isotope Fractionation of Nitrate-Nitrogen and Nitrate-Oxygen

Although numerous studies suggest general causative factors for the distribution of NO_3^- in groundwater (i.e. high N input and well-drained soils), specific dynamics such as nitrogen source availability (e.g. precise amount and type of applied fertilizer) have largely remained an enigma (Spalding and Exner, 1993). This

research assesses nitrogen source availability (amount) and type (animal v. synthetic fertilizer) by utilizing stable isotopes of N and O as a geochemical tracer. The objective was to use the stable isotope ratios $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ in NO_3^- to differentiate NO_3^- in shallow groundwaters resulting from animal and synthetic fertilizer applied to row crops. Records of N source loading were kept in detail during the study period beginning in December of 1999 and are described in the results section.

In previous studies, Bottcher et al. (1990) and Aravena et al. (1993) have shown how use of N isotopes can be applied toward improved understanding of nitrate movement dynamics. Bottcher et al. (1990) illustrated high NO_3^- concentrations are associated with depleted $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values while low NO_3^- concentrations are associated with enriched $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values. Bottcher et al. (1990) traced this pattern from recharge to discharge areas in their study of an aquifer in Germany. Aravena et al. (1993) demonstrated that an isotopic approach with respect to $\delta^{15}\text{N}$ may be based on the premise that the $^{15}\text{N}/^{14}\text{N}$ ratio is larger in animal waste as compared to commercial fertilizers. In the case of $\delta^{18}\text{O}$, synthetic fertilizers are distinguished by very enriched $\delta^{18}\text{O}$ values, because the source of oxygen for these chemicals is atmospheric oxygen (Aravena et al., 1993). More depleted $\delta^{18}\text{O}$ values relative to synthetic fertilizer are expected for nitrate originating from animal wastes (Aravena et al., 1993). A figure depicting typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from various sources is shown in Figure 14.

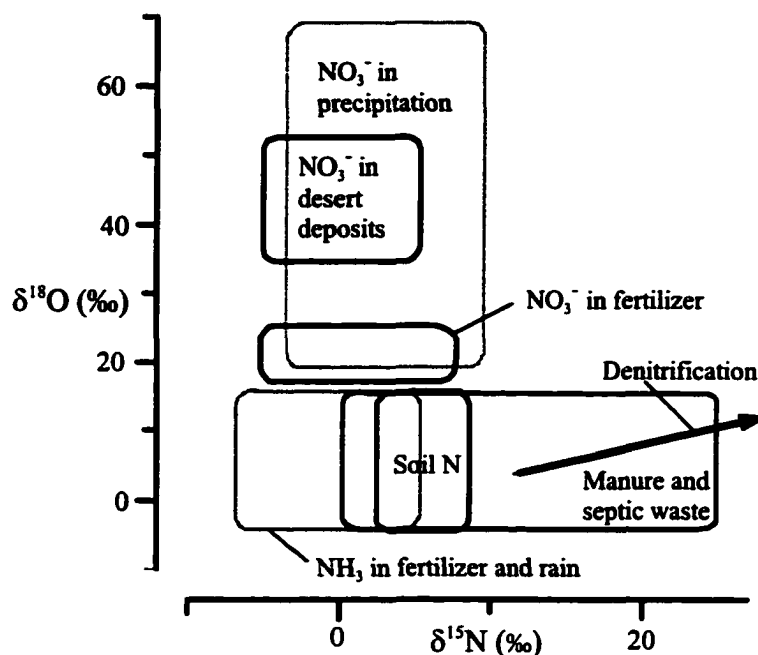


Figure 14. Typical Ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from Various Sources (After USGS, 2000).

Nitrogen isotopes were analyzed by the University of Waterloo EIL and are used to study the chemical behavior of nitrate ion in ground water. Several samples were sent to the EIL in June and July 2000. Additional samples were collected and sent in September and December 2000. Unfiltered samples were collected for nitrate isotope analysis in sterile 500 ml plastic bottles. The bottles were filled to allow enough head space for freezing. The samples then promptly placed in an ice filled cooler and frozen at the end of the day. The samples were shipped overnight in a frozen state to the University of Waterloo the following Monday. Compost and synthetic fertilizer samples were collected in 20 ml scintillation vials.

The isotopic composition of nitrate, determined by mass spectrometry, is expressed in per mil ‰ deviations from a standard. δ notation is defined as

$$\delta \text{ ‰} = (R_{\text{Sample}}/R_{\text{Standard}} - 1) \times 10^3$$

where $R = {}^{15}\text{N}/{}^{14}\text{N}$ and ${}^{18}\text{O}/{}^{16}\text{O}$ of the sample and standard.

The standard utilized for ${}^{18}\text{O}$ was VSMOW. The IAEA and EIL reference used for ${}^{15}\text{N}$ was air.

Sediment Grain Size Analysis and in Situ Denitrification Potential

Soil profile sediment samples were collected in conjunction with installation of the observation wells. Sieve and hydrometer analysis were performed on boring samples to distinguish possible relationships between grain size, nitrate movement, and in situ denitrification potential. Aquifer water chemistry is also considered in this analysis. Francis et al. (1989), in their study of sediment samples collected from the Savannah River Plant, South Carolina, found that surface samples revealed the greatest denitrification response. In the deeper sediments, denitrifying performance was much higher in saturated sandy samples and lower or absent in drier clay samples (Francis et al., 1989). Francis et al. (1989) suggested denitrifying tendency may be limited by insufficient supplies of nitrate in the deep, drier clay samples (1 mg/L NO_3^- or less). In the study reported here, soil profile grain size distribution from surface samples through the saturated zone are analyzed in an effort to refine knowledge of nitrate movement dynamics.

Boring samples were obtained from the auger drill holes. Sediment samples were taken at representative depths during drilling of test wells; that is, cuttings were collected and bagged at noticeable lithologic changes. Two undisturbed samples were obtained by split spoon. Sample color descriptions were noted by comparing color of fresh well cuttings to Munsell soil color charts (1994 revised edition). Forty samples were analyzed for grain-size distribution by mechanical sieving. The hydrometer method was utilized to estimate silt and clay fractions. Investigations were performed at the WMU Rock Preparation Laboratory. The standard test method for particle analysis of soils served as a guide for analysis (ASTM D 422-63). Pore water chemistry parameters analyzed include DO, TOC, NO_3^- -N, and NH_3 , and are discussed in the results section. In addition to grain size analysis, several aquifer sediment samples were analyzed by XRD (x-ray diffraction) to identify specific clay minerals present.

Field Scale Evaluation of the Fate of Agrichemicals with the Immunoassay Test

Herbicides are the only pesticides used by the private farming operation. Chemicals are kept, transferred, and mixed in the tool shed (an outbuilding adjacent to the livestock operations). Herbicide practices varied from 2000-2001. Herbicide use for 2000 consisted of Bicep® (atrazine and metolachlor) for corn, Roundup® (glyphosate) for soybeans, and 2,4-D (2,4-dichlorophenoxyacetic acid) for winter wheat. For 2001, herbicides utilized were Leadoff® (atrazine and dimethenamid) and

Basis® (atrazine, nicosulfuron, and rimsulfuron) for corn and Canopy® (metribuzin and chlorimuron ethyl) and Roundup® for soybeans.

In 2000, Bicep was applied at the rate of 1½ qt/acre, Roundup 1¼ pint/acre, and 2,4-D ½ pint/acre. In 2001, Leadoff was applied at the rate of 2 qts/acre, Basis ¼ oz/acre, Roundup 1 qt/acre, and Canopy 2 oz/acre. A second spray of Roundup was applied at the rate of ½ qt/acre. Bicep was used as a pre-emergent herbicide for corn and sprayed onto the soil. Two weeks before planting, Roundup was applied as a pre-emergent herbicide for beans and sprayed onto the soil. The corn and some beans are row cultivated by tillage which reduces the need to spray herbicides after germination. If it is needed, it is sprayed on but by this time the canopy reduces the loss by wind. No till beans are planted in the spring in fields which have been left as corn stubble over the winter. The 2,4-D herbicide was applied in the spring to wheat at the rate of ½ pint/acre, but only if weedy.

The Michigan Department of Agriculture (MDA) tested samples by immunoassay for specific classes of chemicals beginning June 2000. The tests chosen were 2,4-D, triazine, and alachlor. 2,4-D has not been detected in any samples and will not be discussed further. The USEPA has established a drinking water standard for atrazine of 2 µ/L (USEPA, 1995). Drinking water standards for metolachlor and acetamide have not been established.

Due to the large volume of samples and budgetary constraints, it was deemed immunoassay would be a cost effective method for herbicide analysis. Enzyme linked immunosorbent assay tests are relatively inexpensive (\$15/sample) and widely

used in the environmental field. The immunoassay kits utilized do not differentiate between the various compounds although their presence is detected to differing degrees (Table 5). For example, metolachlor has a LLD (lower limit of detection) of 0.6 ppb. Concentrations below this level indicate metolachlor's metabolite has likely been detected.

Screening by immunoassay makes it economically feasible to analyze many samples. This in turn made GC/MS relatively cost effective since previous immunoassay detection was used as a guideline. GC/MS analysis was used for verification and to distinguish between parent compounds and herbicide breakdown products. Selected water samples collected during the June 2001 sampling event were checked for confirmation by MDA with GC/MS (gas chromatography/mass spectrometry) methods. Selected water samples collected during the July 2001 sampling event were checked for atrazine confirmation only (Kar Laboratories, Inc., Kalamazoo, MI) by GC/MS. Lastly, selected water samples collected during the September 2001 sampling event were analyzed for various corn and soybean herbicides and degradation products (USGS Organic Geochemistry Research Laboratory, Lawrence, KS) by GC/MS and LC/MS (liquid chromatography/mass spectrometry).

In the particular enzyme linked immunosorbent assay (ELISA) method employed, the antibody is immobilized on a solid phase to the inside of a test well. A mixture of a sample which may contain the pesticide of interest, and a enzyme-analog of the analyte is added to the well. After sufficient reaction time, molecules that are

Table 5

**Triazine and Alachlor Immunoassay Listing of Residues Detected
Along with Associated Lower Limit of Detection (LLD*)**

SDI EnviroGard®	Triazine Plate Kit	SDI EnviroGard®	Alachlor Plate Kit
Compound	LLD	Compound	LLD
6-Hydroxy Atrazine	0.30	Alachlor	0.046
Ametryn	0.01	Alachlor ESA	0.13
Atrazine	0.02	Metalaxyl	10
Cyanazine	1.34	Acetochlor	2.5
De-ethylated Atrazine	0.17	Metolachlor	0.6
De-Isopropyl Atrazine	3.5	2-[(2,6-diethylphenyl) (methoxymethyl) amino]-2-oxoethane sulfonic acid	0.08
Prometron	0.01		
Prometryn	0.015		
Propazine	0.013		
Simazine	0.065		
Terbuthylazine	0.15		
Terbutryn	0.24		
Trietazine	0.25		

* All concentrations are in parts per billion (ppb).

not attached to the solid phase are removed by a wash step. Using an enzyme reaction, a colorless substrate is added which is then converted to a colored product. The concentration of the color product will be in direct proportion to the amount of label present and can be quantified in a photometer.

The structure of the organic compound atrazine is shown in Figure 15 while the structure of the organic compound metolachlor is shown in Figure 16. The

IUPAC (International Union of Pure and Applied Chemistry) chemical name for atrazine is 2-chloro-4-ethylamino-6-isopropylamino-s-triazine. The IUPAC chemical name for metolachlor is 2-chloro-N-(2-ethyl-6-methylphenyl)- N-(2-methoxy-1-methylethyl) acetamide.

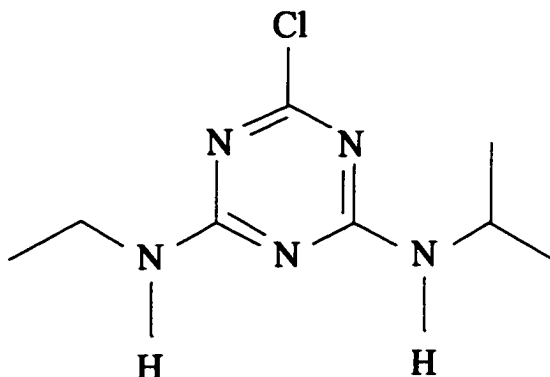


Figure 15. Structure of Atrazine.

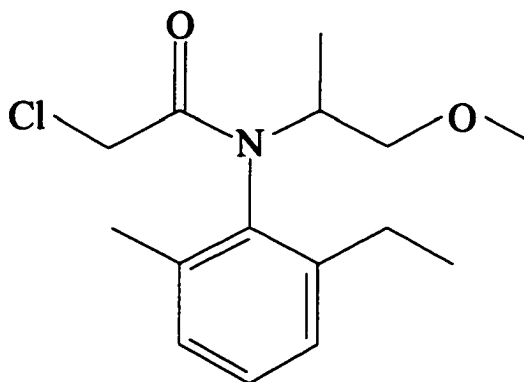


Figure 16. Structure of Metolachlor.

The triazine chemical class forms the basis for several widely used herbicides and consists of 3 atoms of N in the aromatic ring. Metolachlor is one of the chloroacetanilide herbicides.

Some properties that influence phase partitioning of organic compounds are listed in Table 6. As can be seen by the given low vapor pressure values, atrazine and

Table 6

Selected Property Values for Atrazine and Metolachlor (data Hornsby et al., 1996)

	Atrazine	Metolachlor
Vapor Pressure at 25°C (mm Hg)	2.89×10^{-7}	3.135×10^{-5}
Water Solubility (mg/L) at 25°C	33	530
Field half-life (days)	60	90
Sorption Coefficient (K_{oc}) (ml/g)	100	200
Octanol-Water Partitioning Coefficient ($\log K_{ow}$)	2.61	2.51*

* = calculated value

metolachlor have a low potential for volatilization. Other important physiochemical properties listed are water solubility, half-life, and soil sorption coefficient (K_{oc}).

Both atrazine and metolachlor are considered to be soluble with the much more polar nature of metolachlor leading to a comparatively higher solubility (Meyer and Thurman, 1996). Leaching of pesticide compounds to groundwater also depends on rates of degradation and on sorptive properties of the soil to which the compound

was applied (Kehew, 2001). The longer the field half-life the more persistent the pesticide. It is important for herbicides to be decomposed in soil and not transported to surface water because water contains much less organic matter and fewer microorganisms for degradation (Meyer and Thurman, 1996).

The soil sorption coefficient is a measure of the tendency of the herbicide to attach to soil particles. The larger the K_{oc} value the more strongly the pesticide will be adsorbed to soil.

Atrazine is generally regarded as a moderately persistent herbicide (Meyer and Thurman, 1996). The octanol-water partitioning coefficient is defined as the concentration of the compound in octanol divided by the concentration of the compound in water. Nonpolar compounds have high K_{ow} values whereas polar compounds have low K_{ow} values. The estimated log K_{ow} value for metolachlor listed in Table 6 was calculated from a formula described by Karickhoff et al. (1979).

Water samples collected in the June, July, and early Fall (September-October) 2000 sampling events were delivered to MDA for detection of herbicides by the immunoassay test. Unfiltered samples were collected for pesticide analysis in sterile 500 ml plastic bottles. The bottles were filled to allow enough head space for freezing. The samples were promptly placed in an ice filled cooler and frozen at the end of the day. Samples were delivered in a frozen state to the MDA the following day. All water samples collected for analysis followed sampling guidelines, chain of custody protocol, and QA/QC (quality assurance/quality control) plans.

CHAPTER IV

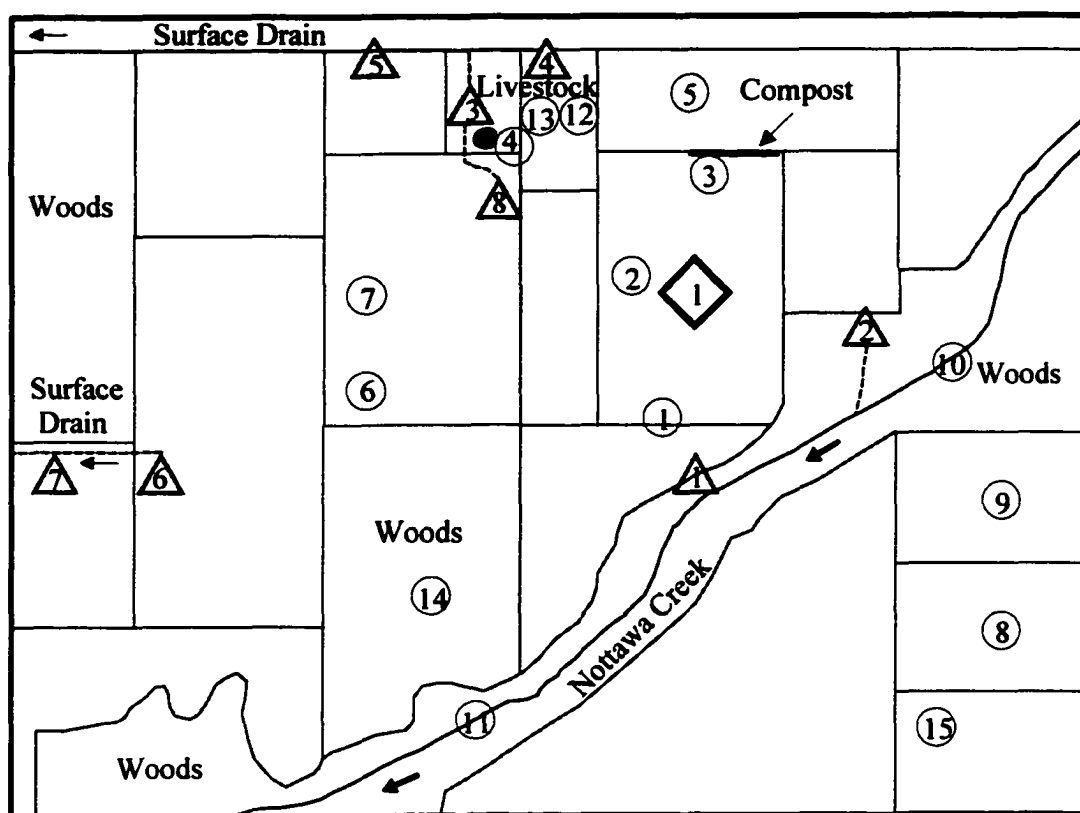
RESULTS AND DISCUSSION

Comparison of Field Scale Model Monthly Infiltration Rates to Estimated Basin Recharge

Two general types of soils typical of the watershed were modeled at the field scale. For simplicity, these are referred to as the Oshtemo (well-drained) and the Brady (somewhat poorly drained) soils. The Brady soil typically requires subsurface drains for agricultural use while the Oshtemo does not (USDA, 1992).

To attempt to understand possible varying infiltration rates for the Oshtemo and Brady soils, field 1 (Figure 17) was employed for two separate simulations. One of the benefits of GLEAMS is the simplicity with which the model can be employed. There is no need to compare separate simulations on fields of varying sizes and slopes. The agricultural management system allows one to model and compare what effect different soil characteristics may have on a particular field.

Lithology of the soils was distinguished by studying drill cuttings from observation wells. The water table is approximately 6 feet deep. The Brady soil was partitioned into 2 layers for the model; a sandy loam (30 cm) and a fine sandy loam (152 cm). Soil characteristics were chosen from the CREAMS user guide and



EXPLANATION

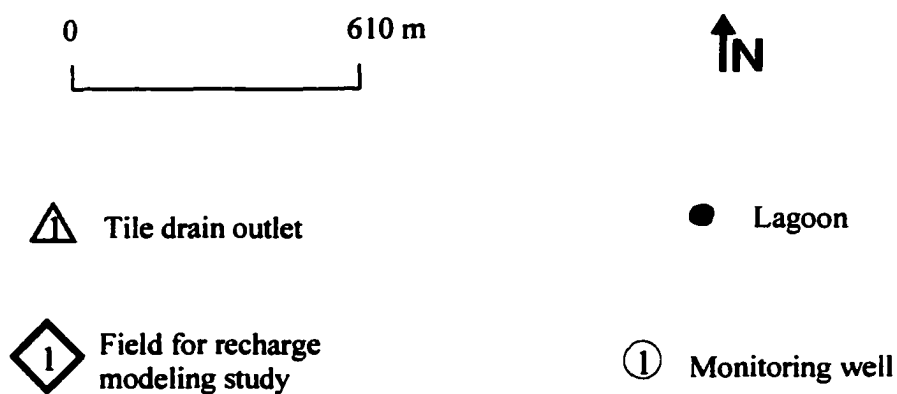


Figure 17. Schematic of Study Area and Field Utilized for Recharge Model Study.

computer model guidance suggestions, and the Soil Survey of Calhoun County, Michigan (USDA, 1992). For example, porosity was respectively 0.46 and 0.48. Kutilek and Nielsen (1994) cite ranges of porosity from 0.30 to 0.55 for loamy soils whereas Heath (1983) cites a selected value of 0.55 for soil porosity. Selected field capacity values were 0.19 and 0.22. Saturated hydraulic conductivity values were calculated according to Stephens (1995) as 3.3 cm/hr respectively for both layers.

The Oshtemo soil was likewise partitioned into 2 layers for the model; a sandy loam (30 cm) and a coarse sand (152 cm). For the Oshtemo soil, porosity was assigned values of 0.40 and 0.40. Field capacity values were designated as 0.16 and 0.11. Saturated hydraulic conductivity values were again estimated from Stephens (1995) as 3.6 cm/hr and 11.4 cm/hr respectively. The hydraulic slope of the field (0.009) was calculated from the USGS Union City quadrangle.

Input of climatic factors included average daily temperature for January 1999-September 2001 from weather stations Athens and/or Ceresco as described in the methods section. Precipitation likewise was input as daily variables for January 1999-September 2001. In addition, mean monthly solar radiation, mean monthly wind movement, and mean monthly dew point were input for each month.

The program was run for 3 years. Grain corn was planted on May 11 and harvested November 1 for each of the three years. The program option selected was winter weeds after harvest. In other words, the field lay fallow in lieu of a cover crop after harvest. The crop rooting depth was allowed to reach 61 cm. It was assumed the field was saturated at the beginning of the simulation because of cooler

temperatures and the lag time of two months after the harvest date.

A study by Holtschlag (1997) of groundwater recharge for the Nottawa Creek drainage basin served as a comparison model. Before presenting the results for the field scale study, the quantitative methods employed by Holtschlag (1997) will be briefly summarized.

A recharge rate for the Nottawa Creek drainage system was estimated by Holtschlag (1997) utilizing a hydrograph separation technique in conjunction with analysis of a 24 year record of streamflow gaging station data and precipitation. The specific hydrograph separation technique is referred to as streamflow partitioning (Holtschlag, 1997). In addition to the hydrograph separation technique, a set of regression equations was also developed utilizing precipitation data from available stations within the area (Holtschlag, 1997). With this particular method, normal basin recharge rates were calculated to relate annual variations in groundwater discharge to annual variations in precipitation and the previous year's groundwater discharge (Holtschlag, 1997). By way of comparison, the average annual estimated recharge rate for the Nottawa Creek drainage system is 28.98 cm/yr while the normal estimated recharge rate is 27.43 cm/yr (Holtschlag, 1997).

The results of the 1999 field scale simulation for the two soil types are listed for comparison in Table 7. The simulations imply the Oshtemo soil likely provides higher recharge rates than the Brady soil. By comparison, the annual recharge results are lower than estimated by Holtschlag (1997). This may be due to land cover and soil type differences utilized in Holtschlag's (1997) model. Another reason for

Table 7

1999 Monthly Summary of Simulation Results (cm)

	Total Precipitation	Brady Recharge	Oshtemo Recharge
January	5.64	2.71	2.80
February	3.63	1.83	1.89
March	1.29	0.77	0.79
April	17.37	3.19	3.48
May	5.38	0.22	0.22
June	14.68	6.25	6.25
July	5.00	0.21	0.21
August	8.23	0	2.78
September	7.24	0	0.27
October	3.15	0	0
November	5.26	0	0.54
December	3.35	0	1.97
Total	80.22	15.18	21.20

recharge differences may be due to weather patterns. Total precipitation for 1999 was 80.2 cm as reported by the Athens weather station, whereas the normal is considered to be 90.7 cm. It is typically assumed most recharge occurs during spring and fall because evapotranspiration is at a minimum and the ground is not frozen. Precipitation records for the Athens station indicate the fall of 1999 was atypically dry (Figure 18), which may also help explain the low recharge rates for the fall of 1999.

The water levels in observation wells for 1999 were measured only once (December 11-12). Observation well water levels as depicted in Figure 19 seem to support the notion recharge may be correlated with precipitation and saturation.

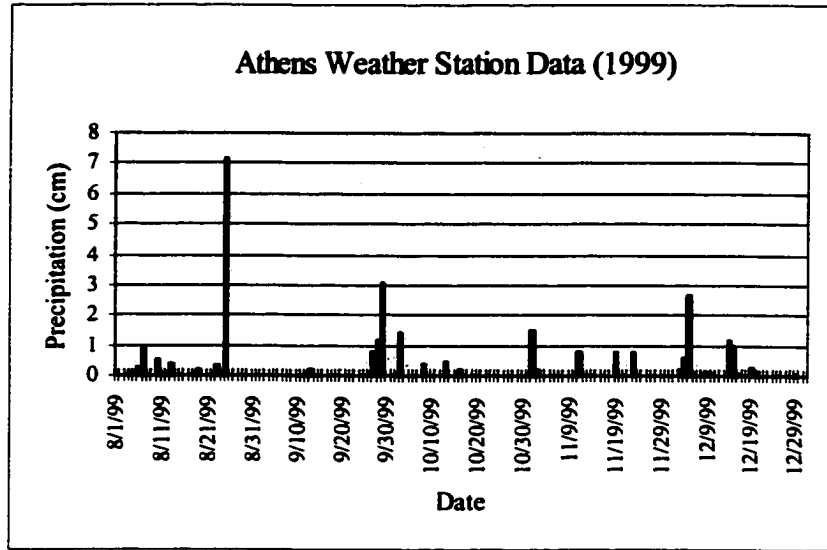


Figure 18. August-December 1999 Total Precipitation.

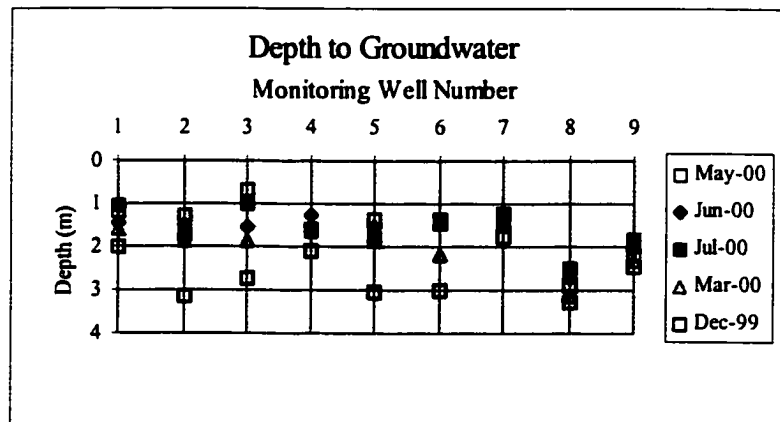


Figure 19. Observation Well Water Levels December 1999-July 2000.

The results of the field scale simulation for 2000 are listed in Table 8. For the period listed, the model actually shows most recharge occurred during June for the Brady soil and September for the Oshtemo soil. The recharge rate for the year, about 40 and 48 cm, respectively, for the Brady and Oshtemo soils are higher than the

Table 8

2000 Monthly Summary of Simulation Results (cm)

	Total Precipitation	Brady Recharge	Oshtemo Recharge
January	2.97	0	2.09
February	2.74	1.24	1.34
March	4.78	0.59	0.65
April	9.04	5.49	5.51
May	15.44	7.91	7.91
June	18.24	10.11	10.15
July	6.78	0	0
August	12.75	0	2.29
September	16.92	6.98	10.84
October	6.96	3.22	3.22
November	6.40	4.05	4.05
December	1.07	0.42	0.44
Total	104.09	40.01	48.49

USGS model of about 30 cm. Again, weather patterns were atypical for 2000 as total precipitation was 13.5 cm above the norm as reported by the weather stations. A graph of Athens weather station data from January to July of 2000 tends to substantiate the simulation of recharge by the model for that time period (Figure 20).

The results of the field scale simulation for 2001 are listed in Table 9. The study ended in September and results are shown only through the end of the month. For the period listed, the model simulation shows most recharge occurred during May. Observation well water levels measured in June likely reflect May recharge (Figure 21). Recharge rates seem low for August and September. Knisel (1980) states that the program may underestimate recharge rates. On the other hand, the

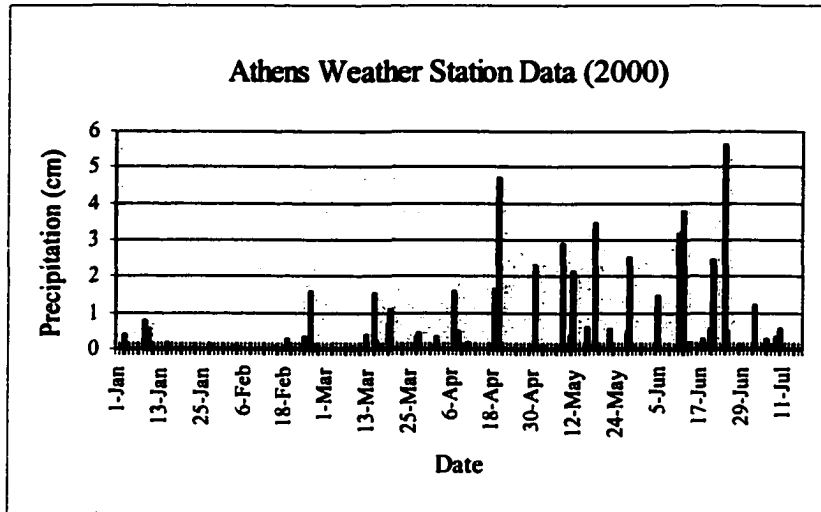


Figure 20. January-July 2000 Total Precipitation.

Table 9

2001 Monthly Summary of Simulation Results (cm)

	Total Precipitation	Brady Recharge	Oshtemo Recharge
JAN	3.45	1.91	1.97
FEB	8.66	3.59	3.74
MAR	1.30	0	0
APR	6.40	0.19	0.29
MAY	15.34	7.48	7.48
JUN	8.10	1.12	1.12
JUL	8.97	0.99	1.32
AUG	12.14	0	1.31
SEP	11.73	0	1.10
TOT	76.09	15.28	18.33

program provides an estimate of soil water uptake requirements for corn at certain leaf stages along with soil evaporation estimates.

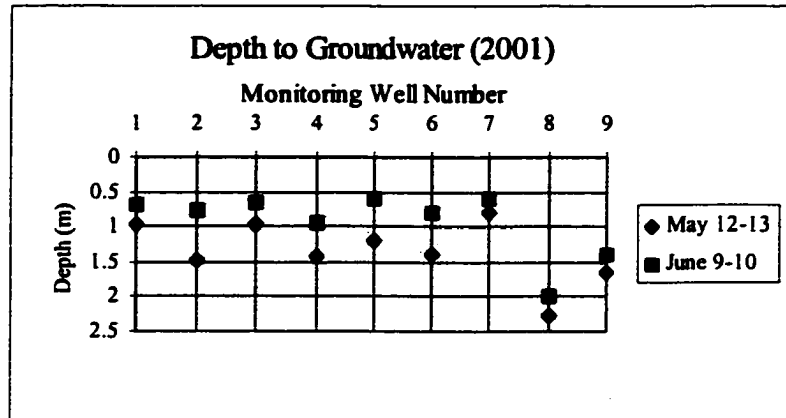


Figure 21. Observation Well Water Levels May and June 2001.

Sources of error for simulation outcomes include lack of input of storm frequency and intensity. Although GLEAMS does contain a program option for storm events, precipitation data was reported on a daily basis only for the Athens and Ceresco weather stations. Stephens (1996) noted that with water balance methods based on field capacity, the calculated recharge is likely underestimated when recharge is a small fraction of precipitation and the period of water balance accounting is too long. Thus, recharge may be underestimated during periods of summer thunderstorms common within the study area. Another source of error is preferential flow routes, which if present could have dramatic effects on recharge.

A BASIC Triangular Finite Element Groundwater Flow Model

The finite element grid developed for groundwater flow is shown in Figure 22. The grid consists of 98 nodes and 164 elements and represents an area of

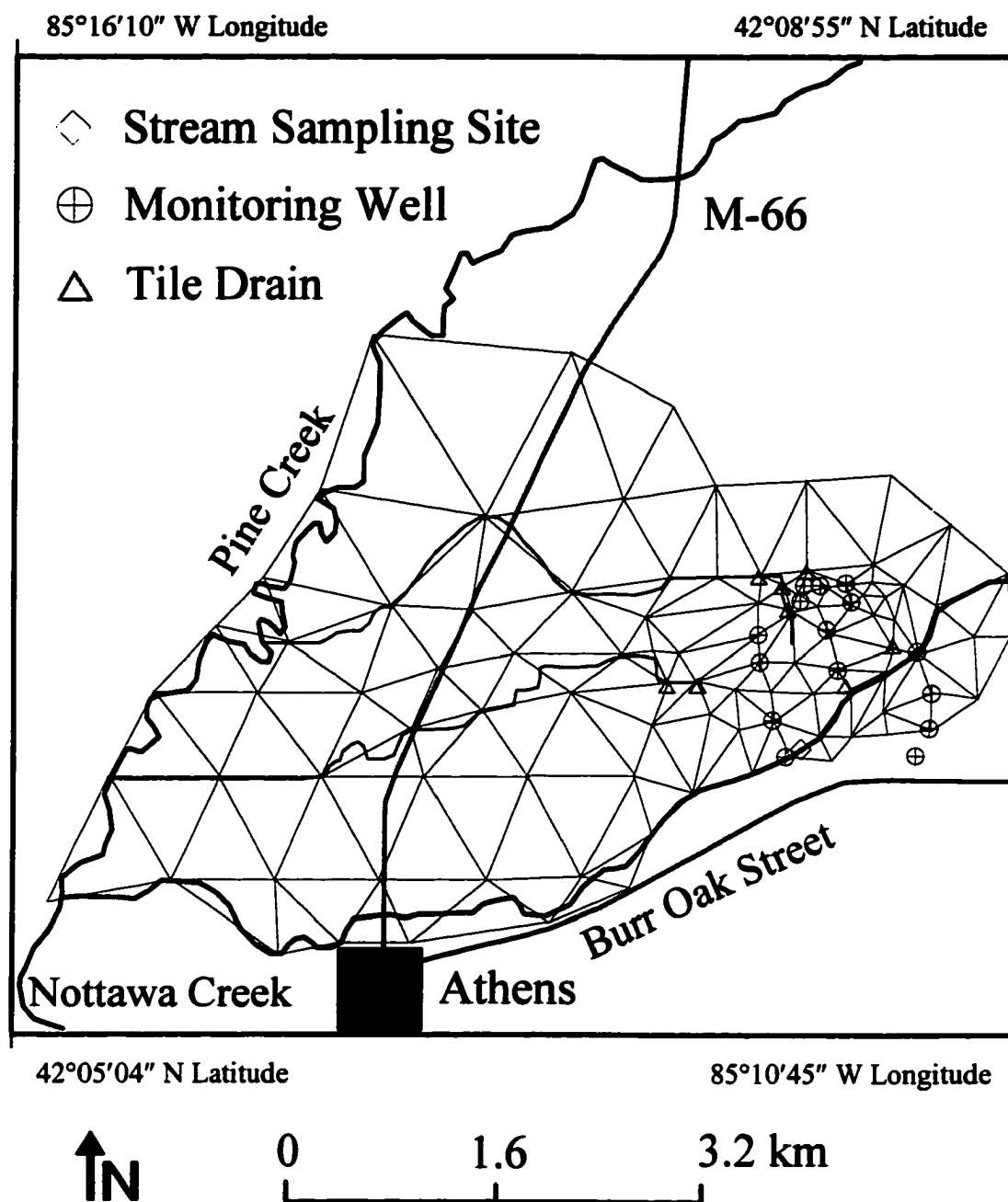


Figure 22. The Finite Element Grid Used for the Groundwater Flow Model.

approximately 7.8 km². It is a one layer model for the unconsolidated aquifer. The groundwater system is assumed to be at steady state.

Input files for the model require nodal coordinate position, head and head type, and a recharge or discharge value, whereas the elemental file requires the node numbers and a transmissivity value. Local hydraulic conductivity values were estimated from a grain size analysis for observation wells within the water quality study area. Regional hydraulic conductivity values were estimated as 15 m/day, a value for medium sand (Heath, 1982). Selected horizontal hydraulic conductivities for the model ranged from 3×10^{-3} m/day to 107 m/day. Aquifer thicknesses ranged from 1.5 to 12.2 m and were estimated from this research and previous studies (Moser and Passero, 1990; Kozlowski, 1999). Static water elevations from a glacial drift water well survey (Moser and Passero, 1990) were compared to a bedrock elevation map (Kozlowski, 1999) to determine aquifer thicknesses for elements. Selected transmissivity values ranged from 0.053 to 75.6 cm²/sec. A recharge value of 27.4 cm/yr (8.5×10^{-7} cm/sec) as estimated by Holtschlag (1997) was utilized. This value was preferred to the site specific recharge values (see Tables 7-9) because it represents a 24 year average. In this model, the stream nodes were labeled as the only constant heads and it is assumed that groundwater discharges into the streams. Based on a USGS study (Holtschlag, 1997), this seems to be a justifiable assumption. Stream elevations were estimated from USGS quadrangle maps. Tile drain outlets were designated as discharge nodes with a selected value of 1.5 cm/sec. This is an

arbitrary rate and was estimated by trial and error during model calibration by matching measured and simulated monitoring well heads.

The two-dimensional groundwater flow model calculates the elevation of the water table for the unconsolidated aquifer. A contour map constructed from simulation of groundwater flow is shown in Figure 23 and suggests groundwater in the study area flows towards both Pine Creek and Nottawa Creek. The groundwater flow simulation supports the notion implied from the conceptual model of a groundwater divide within the study area (see Figure 6). Chloride levels also support the existence of a groundwater divide. If chloride is assumed to react as a conservative constituent, chloride concentrations would be expected to increase downgradient. However, the chloride concentrations detected from MW-7 were always significantly larger than in MW-6 indicating groundwater does not flow from MW-7 to MW-6.

Calibration of groundwater flow models normally involves comparison of measured heads with model-calculated heads. The groundwater flow model may only reinforce the notion of a groundwater divide in the study area in lieu of being a predictive tool of groundwater heads. Simulated heads were as much as 3 m below field measured heads. Still, since groundwater flows in the direction of total head, the model simulation may be a fairly accurate indicator of direction of groundwater flow.

Sensitivity analysis normally involves varying one or more input variables with all other model input values held constant. Regarding sensitivity analysis, the model is most sensitive to recharge variations. In fact, varying recharge by a factor of

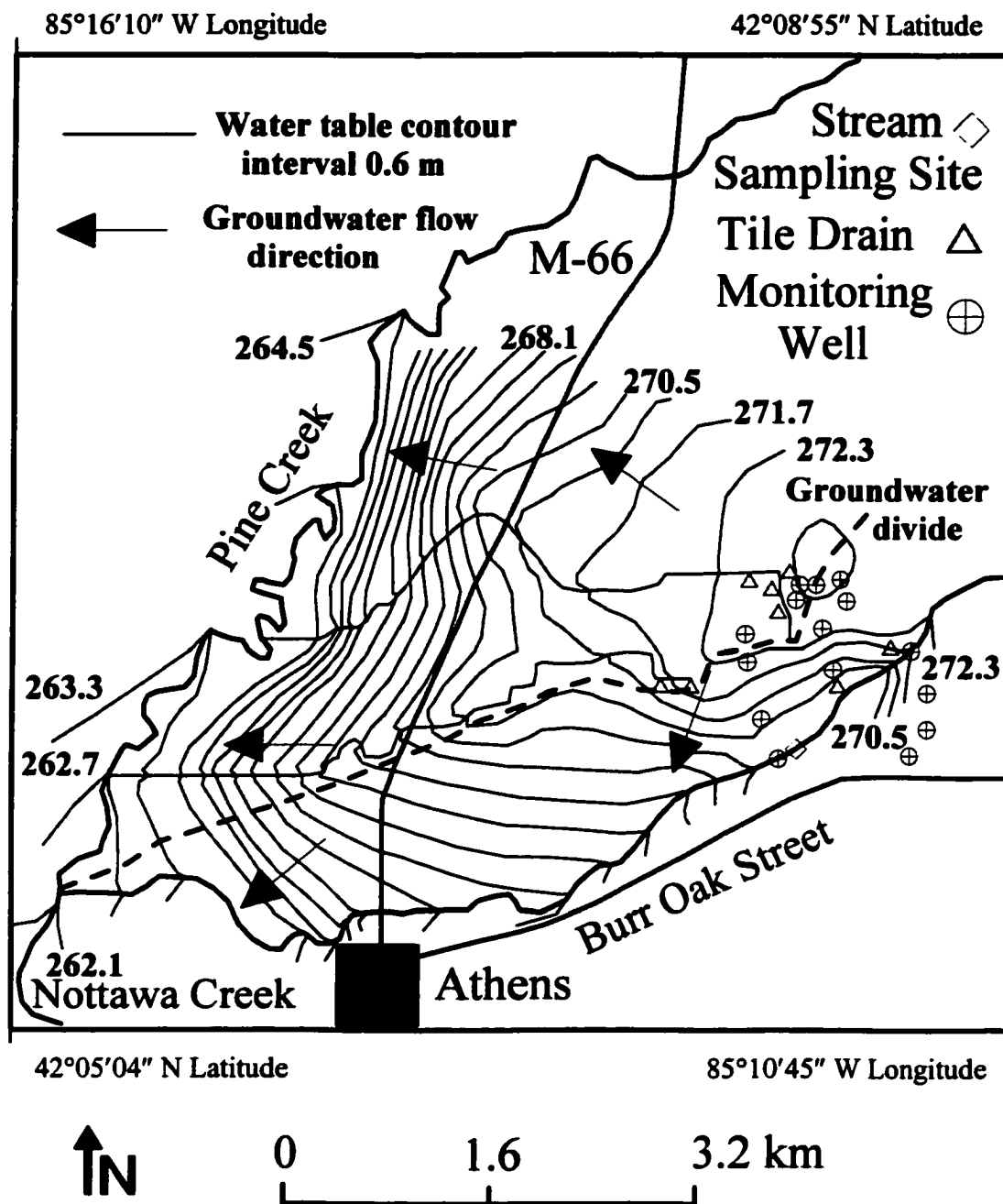


Figure 23. Water Table Map Generated by a Groundwater Flow Model.

10 raised some simulated heads to near field measured head values although some values were abnormally high. Transmissivity sensitivity analysis was not performed due to lack of detailed regional data.

In summary, groundwater in the study area appears to discharge both to Nottawa Creek and Pine Creek. The model is restricted by the limited capacity of data available and should be viewed within the limitations and assumptions described.

Spatial and Temporal Geochemistry Trends in Groundwater, Agricultural Drains, and Surface Water

A water quality sampling program provided testing for selected private wells, monitoring wells, tile drains, and Nottawa Creek surface water as previously described. Results for each sampling event are listed individually in Appendix B.

Charge Balance Error and Duplicates

Part of the quality assurance/quality control (QA/QC) program consisted of calculating charge balance error to document the reliability of the chemical analysis. Duplicate samples from the same source were occasionally submitted for analysis to account for laboratory precision. The cation-anion charge balance is expressed here as a percentage by the following equation:

$$\text{Charge Balance Error} = \frac{(\sum \text{Cations} - \sum \text{Anions})}{(\sum \text{Cations} + \sum \text{Anions})} \times 100$$

where ions are in units of meq/L. Because the solution must be electrically neutral, the analysis is assumed to be reliable if the balance is less than 5% (Hounslow, 1995). If the balance is greater than 5% the analysis is inaccurate, or cations or anions are present in significant quantities that were not used to calculate the balance. The percentage value is positive if the cations are larger or negative if the anions are larger.

The use of charge balance as a reliability check on completeness and quality may not be practicable if organic acids are present in significant quantities. For example, Owen and Manning (1995) state that humic and fulvic acids contribute to titrated alkalinity. Lastly, because alkalinity was not measured in the field for this study, alkalinity values may be erroneously low because of calcium carbonate precipitation before analysis. This results in a low bicarbonate measurement. Positive charge balance errors are more common for alkalinity analyses measured in the lab (Kehew, 2001). The charge balance errors calculated for the study are listed in Table 10.

Five duplicate samples were collected for analysis over the course of the study and submitted in a way so the lab did not know which samples were duplicates. The precision percentage of the duplicate constituents was averaged and lies within a range of $\pm 10\%$ except for the following: $\text{Na} \pm 12\%$, $\text{NO}_3^- \text{-N} \pm 24\%$, $\text{TOC} \pm 29\%$, and $\text{Total P} \pm 31\%$. Accuracy and reproducibility for determinations of constituents below 1 mg/L is generally not better than $\pm 10\%$ and can be less Hem (1985).

Table 10

Percent Charge Balance Error Calculated for the Study

	Dec. 1999	Mar. 2000	Jun. 2000	Oct. 2000	Dec. 2000	Mar. 2001	Jun. 2001	Sep. 2001
MW-1	---	14.7	16.0	9.1	4.0	5.6	-2.1	8.1
MW-2	---	2.1	-0.1	0.5	1.9	3.1	-2.6	-2.4
MW-3	1.6	4.0	5.8	7.3	6.8	6.0	4.5	4.3
MW-4	7.2	14.2	15.3	11.9	15.7	19.2	16.2	9.8
MW-5	6.8	21.2	-2.8	7.3	4.9	3.3	1.7	---
MW-6	---	14.8	14.3	14.0	15.7	14.3	17.4	19.0
MW-7	26.5	-0.2	1.0	2.5	2.7	1.6	-0.1	5.3
MW-8	1.5	-1.6	3.8	10.0	11.5	13.4	6.4	10.9
MW-9	-1.1	-1.6	-31.3	-0.7	2.2	0.7	1.5	2.1
MW-10	---	---	4.2	1.2	2.1	4.0	-0.05	1.9
MW-11	---	---	4.0	-0.9	2.3	0.7	-1.8	-0.8
SW-1	0.4	0.3	5.2	2.2	3.4	4.1	0.9	4.1

--- no calculation

No results are discounted in the following reporting and discussion of chemical data. Although some charge balance errors are over 5%, it may only indicate that an analysis is unusual and not necessarily wrong (Hounslow, 1995). For example, MW-4 consistently had TDS concentrations of 2000 mg/L or greater. In waters with TDS concentrations such as these, the cation-anion balance test does not sufficiently measure the value of the lesser constituents (Hem, 1985).

Major Ion Chemistry

The major or common ions for the purpose of this discussion refer to calcium, magnesium, sodium, potassium, bicarbonate, sulfate, and chloride. The major ion chemical data from June 2000, when plotted on a Piper plot, indicate most of the

waters are a calcium-magnesium bicarbonate type with MW-4 and MW-5 results lying outside of the general cluster (Figure 24). MW-4 is next to an animal waste lagoon and MW-5 is the deepest monitoring well (~ 8 m) and on a topographic high.

A fingerprint diagram for major ions is shown in Figure 25 along with a table of values (Table 11). Nottawa Creek surface water (SW-1) is very similar chemically to the monitoring wells indicating baseflow is a major component of total stream flow. MW-4, the well adjacent to the animal waste lagoon is distinctly different chemically. The potassium concentration value of 433 mg/L for MW-4 is abnormally high for potassium concentration in groundwater. A sample collected directly from the lagoon was reported to contain 3.8 kg of K_2O per 3.8 m^3 (University of Wisconsin Soil and Forage Analysis Laboratory, 2000).

The major ion chemical data from for the tile drains likewise indicate the waters are a calcium-magnesium bicarbonate type. TD-5 could not be filtered in the field and consequently was not sampled for metals.

A statistical summary for the major ion chemical data for monitoring wells and tile drains is shown in Tables 12 and 13. MW-4 consistently had the largest concentration values for individual major ions. This is not surprising since the well is situated adjacent to the lagoon. Excluding MW-4 test results, other individual parameters will now be discussed.

Calcium concentration values for monitoring wells varied from a minimum of 35.4 mg/L for MW-5 (June 2000) to a maximum of 114 mg/L for MW-7 (Dec. 1999). Calcium concentration values of 60-100 mg/L would not be expected to be

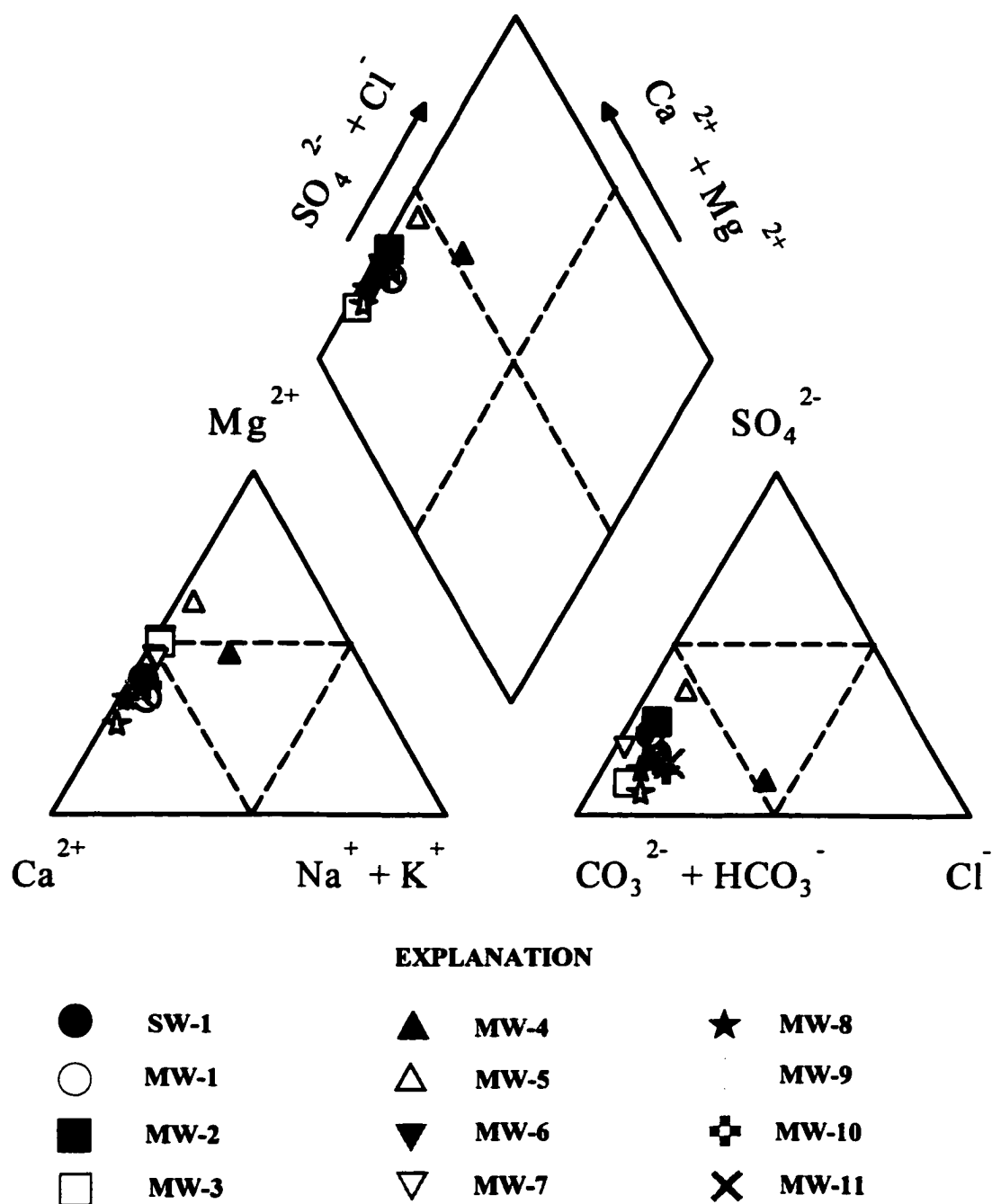


Figure 24. Piper Diagram of June 2000 Results (Concentrations Plotted in meq/L).

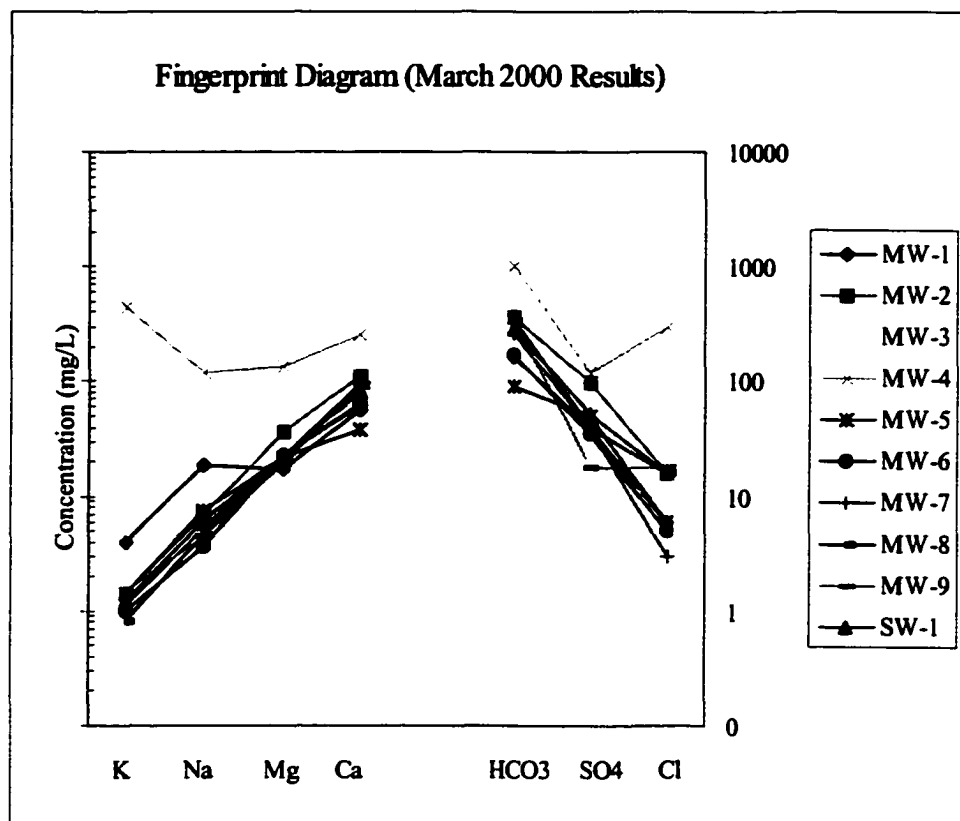


Figure 25. Major Ion Fingerprint Diagram.

Table 11

March 2000 Major Ion Chemical Data (mg/L)

	K	Na	Mg	Ca	HCO ₃	SO ₄	Cl
MW-1	4	18.8	16.8	55.3	161	39	6
MW-2	1.4	6.8	35.7	112	366	98	16
MW-3	1.4	5.4	26.1	70.4	290	21	8
MW-4	433	120	132	250	1016	121	291
MW-5	1.4	7.5	21.6	38.1	89	50	6
MW-6	1	3.7	22.5	64.1	169	35	5
MW-7	1.1	5.2	22.3	61.3	261	39	3
MW-8	0.8	4.6	21.7	95.7	348	39	16
MW-9	1.5	4.4	19.5	90.5	350	18	18
SW-1	1.2	6.2	22.4	80.9	280	52	16

Table 12

Monitoring Well Statistical Summary for Major Ions (mg/L)

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
Ca - #	7	7	8	8	7	8	8	8	8	6	6	8
Avg.	63.5	101	81.0	199	46.2	64.0	72.3	85.8	88.3	89.9	103	82.8
Median	62.5	98.0	81.2	194	43.7	64.6	67.0	82.6	92.6	88.6	103	81.2
Max	74.7	112	101	250	61.3	65.6	114	103	96.6	96.4	107	89.4
Min	55.3	88.9	66.8	165	35.4	61.2	61.3	75.7	50.6	85.8	99.7	77.2
St.Dev.	6.2	8.8	10.9	29.2	9.6	1.6	17	9.7	15.4	4.1	3.3	4
Mg - #	7	7	8	8	7	8	8	8	8	6	6	8
Avg.	14.9	35.6	29.4	94	30.5	19.6	24.2	18.1	17.8	23.9	22.9	21.9
Median	15.7	35.7	30.3	88	33.5	20.6	22.6	17.2	19.3	23.7	22.9	22.2
Max	17.3	39.6	33.8	132	37.1	22.5	34.2	21.7	20.2	24.9	23.8	24.8
Min	11.9	30.9	23.4	73	21.6	10.4	22.3	15.8	6.9	23.2	22.2	18.9
St.Dev.	2	3.4	3.4	23.3	5.9	3.9	4.1	2	4.4	0.7	0.6	1.8
Na - #	7	7	8	8	7	8	8	8	8	6	6	8
Avg.	13.6	5.8	4.8	74.2	5.2	3.2	4.5	3.7	4.4	11.0	10.8	5.7
Median	11.7	5.7	4.6	65.1	5.5	3.2	4.5	3.8	4.6	11.7	10.7	5.7
Max	24.6	6.8	6.2	120	7.5	3.8	5.9	4.6	5.2	13.4	11.5	6.5
Min	6.9	4.5	3.7	44.6	3.4	2.3	3.5	2.4	2.9	6.7	10.1	5.0
St.Dev.	6.2	0.8	0.8	25.9	1.4	0.6	0.8	0.6	0.7	2.5	0.6	0.6
K - #	7	7	8	8	7	8	8	8	8	6	6	8
Avg.	3.2	1.3	1.5	340	1.1	0.7	1.2	0.8	1.5	1.2	1.8	1.3
Median	3.4	1.2	1.6	325	1.1	0.6	1.2	0.8	1.6	1.2	1.8	1.3
Max	4.0	1.7	1.9	433	1.4	1.1	1.3	0.9	1.8	1.4	2.0	1.6
Min	1.9	0.9	1.3	269	0.9	0.4	1.0	0.7	0.4	1.0	1.7	1.2
St.Dev.	0.8	0.3	0.2	54.5	0.2	0.3	0.1	0.1	0.4	0.2	0.2	0.2
HCO₃#	7	7	8	8	7	8	8	8	8	6	6	8
Avg.	198	366	307	809	176	164	267	258	344	320	357	280
Median	192	366	312	811	181	168	270	246	347	323	361	282
Max	246	395	329	1016	236	179	274	348	359	329	369	305
Min	161	324	289	628	89	145	257	203	325	302	341	245
St.Dev.	33.3	27.0	15.8	132.3	50.3	11.1	6.4	54.7	11.1	10.1	10.5	18.8
SO₄ - #	7	7	8	8	7	8	8	8	8	6	6	8
Avg.	38	87	18	108	68	29	39	23	18	40	46	42
Median	36	83	19	114	68	30	40	21	18	38	47	41
Max	46	100	22	130	79	35	43	39	25	48	51	52
Min	34	70	8	62	50	24	35	13	8	35	39	37
St.Dev.	4.1	11.3	4.6	20.9	9.3	4.7	2.4	9.6	5.2	5.8	4.4	5.3
Cl - #	7	7	7	8	7	8	8	8	8	6	6	8
Avg.	5	13	20	179	9	6	2	12	18	20	28	16
Median	5	14	15	154	10	6	2	13	18	21	28	16
Max	6	16	56	291	11	7	3	16	19	24	29	17
Min	4	9	8	104	6	5	2	6	16	14	26	14

Table 13

Tile Drain Statistical Summary of Major Ions (mg/L)

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	SW-1
Ca - #	3	3	3	6	0	4	3	4	8
Avg.	64.5	64.2	78.5	78.7		64.3	75.1	132	82.8
Median	73.9	60.2	79.4	80.7		64.2	76.3	126.5	81.2
Max	75.1	73.7	79.4	84.6		70.0	86.3	160	89.4
Min	44.4	58.7	76.8	65.6		58.8	62.6	115	77.2
St.Dev.	17.4	8.3	1.5	6.9		4.7	11.9	21.2	4
Mg - #	3	3	3	6	0	4	3	4	8
Avg.	17.2	17.9	21.6	21.5		19.8	23.0	29.6	21.9
Median	18.6	16.6	21.3	22.3		20.05	22.5	29.1	22.2
Max	21.5	20.7	22.8	24.0		20.8	24.4	35.4	24.8
Min	11.4	16.3	20.8	16.8		18.4	22.2	24.8	18.9
St.Dev.	5.2	2.5	1.0	2.6		1.1	1.2	4.6	1.8
Na - #	3	3	3	6	0	4	3	4	8
Avg.	3.3	3.1	3.1	8.0		4.6	2.8	16.1	5.7
Median	3.2	3.0	3.2	8.0		3.8	2.8	16.4	5.7
Max	4.6	3.5	3.7	9.5		7.4	3.7	20.6	6.5
Min	2.0	2.8	2.5	6.7		3.3	1.9	11.1	5.0
St.Dev.	1.3	0.4	0.6	1.0		1.9	0.9	5.0	0.5
K - #	3	3	3	6	0	4	3	4	8
Avg.	2.0	0.9	0.7	4.3		0.8	0.8	1.8	1.3
Median	2.1	0.8	0.97	4.25		0.79	0.82	1.9	1.22
Max	3.0	1.2	1.0	7.5		1.02	0.91	2.0	1.6
Min	0.8	0.6	0.08	1.8		0.6	0.6	1.4	1.2
St.Dev.	1.1	0.3	0.5	1.9		0.2	0.2	0.3	0.2
HCO₃ - #	7	3	4	7	3	7	6	7	8
Avg.	123	149	243	216	185	197	251	301	276
Median	115	134	245	211	181	203	245	292	282
Max	169	178	257	244	200	208	296	347	295
Min	92	134	224	195	173	176	234	262	239
St.Dev.	28.7	25.4	14.6	21.0	13.9	12.5	23.1	28.2	17.7
SO₄ - #	7	3	4	7	3	7	6	7	8
Avg.	24	20	38	32	34	34	35	14	41
Median	23	19	40	30	33	36	36	13	41
Max	33	26	40	39	36	43	46	19	52
Min	19	16	33	25	32	23	20	10	30
St.Dev.	4.9	5.1	3.5	5.4	2.1	7.0	9.7	3.9	6.5
Cl - #	7	3	4	7	3	7	6	7	8
Avg.	7	8	11	31	9	10	9	122	15
Median	7	8	11	29	8	8	10	110	15
Max	10	9	11	40	10	16	13	197	17
Min	6	6	10	28	8	6	5	100	14

unusual for this area due to carbonate minerals present in the drift and an occasional application of agricultural lime. MW-5 also had the lowest average of calcium concentration values. As stated previously, MW-5 is the deepest (~ 8 m) monitoring well and is situated on a topographic high. The comparatively low calcium concentration values for MW-5 could be due to a high CEC as a soil profile grain size analysis (see Appendix A) indicated these stratigraphic layers contained a relatively high proportion of clay. The higher the CEC, the higher the negative charge and the more cations that can be held. Although MW-10 and MW-11 were not tested until June of 2000 and hence were excluded on the major ion fingerprint diagram (see Figure 25), the calcium results are very similar to Nottawa Creek surface water (SW-1) indicating baseflow is a major component of total stream flow.

The calcium concentration values for tile drains were very similar, varying from an average of 64.2 mg/L for TD-2 to an average of 78.7 mg/L for TD-4. The average calcium concentration value for TD-8 of 132 mg/L was significantly different. This could be due to relatively lower amounts of clay and organic matter present in the soil.

Magnesium concentration values did not show clear spatial or temporal variations for either the wells or tile drains. Magnesium may be expected to correlate with calcium due to similar chemical properties. However, for monitoring wells, the correlation coefficient value for calcium and magnesium for June 2000 was 0.4, which was too low for the criteria selected for a strong correlation (0.6). On the other hand, for tile drains, the correlation coefficient value for calcium and magnesium for

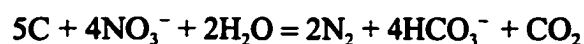
June 2000 was 0.82. This may be due to magnesium-bearing minerals being more susceptible to weathering near the surface, with leaching subsequently preferentially intercepted by tile drains. Nottawa Creek surface water likewise exhibited little seasonal variation in magnesium concentration values.

Average sodium concentration values for monitoring wells ranged from 3.2 mg/L for MW-6 to 13.6 mg/L for MW-1. It is possible cation exchange with the sodium-montmorillonite bentonite seal is responsible for the anomalous sodium concentration values for MW-1. Although the granular bentonite seal was placed above the screen, the water table occasionally rose above the screen. Another possibility is the very shallow shale bedrock (see Appendix A) may be higher in sodium than the glacial sediments. The sodium concentration values for other monitoring wells were very similar, both spatially and temporally, except for the streambed wells. MW-10 and MW-11 average sodium concentration values were 11.0 and 10.8 mg/L respectively. These values may be reflective of the longer flow paths and hence groundwater residence times. Discharge from bedrock might be a factor here as well. Nottawa Creek surface water showed very little variation in sodium concentration with an average value of approximately 5.7 mg/L. The sodium concentration values for tile drains varied from an average of 2.8 mg/L for TD-7, a small single drain, to an average of 16.1 mg/L for TD-8. The largest temporal variation of sodium concentration values was for TD-8, which ranged from 11.1 (June 2000) to 20.6 mg/L (September 2001).

Average potassium concentration values for monitoring wells ranged from 0.7

mg/L for MW-6 to 3.2 mg/L for MW-1. Again, MW-1 is the most shallow well, which may account for the high concentration value as potassium is not considered very mobile. Nottawa Creek surface water average potassium concentration values of 1.3 mg/L showed little variation in concentration over time. Average potassium concentration values for tile drains ranged from 0.7 mg/L for TD-3 to 4.3 mg/L for TD-4. Livestock operations are within the area of influence of tiles for TD-4 which may account for the relatively high reported potassium concentration values. Neither the wells or tile drains showed clear spatial or temporal variations for potassium concentration values.

Bicarbonate was the dominant anion for monitoring wells with average bicarbonate concentration values ranging from 164 mg/L for MW-6 to 366 mg/L for MW-2. Bicarbonate increases as water enriched in CO₂ causes dissolution of carbonate minerals, in the process raising pH. A composition diagram for calcium and bicarbonate is illustrated in Figure 26. MW-9 is plotted as an outlier on the graph indicating the water is distinctly different from the others. The regression line excludes MW-9. MW-8 is 150 m upgradient from MW-9 and had a nitrate concentration value of 3.3 mg/L for June 2000, whereas MW-9 had a nitrate concentration value of 0.57 mg/L. Nitrate reduction may be occurring along the flow path as can be represented by the following reaction:



where C represents an organic compound with an oxidation state of zero (Korom, 1992). This could help account for the increase in bicarbonate for MW-9 without a corresponding increase in calcium.

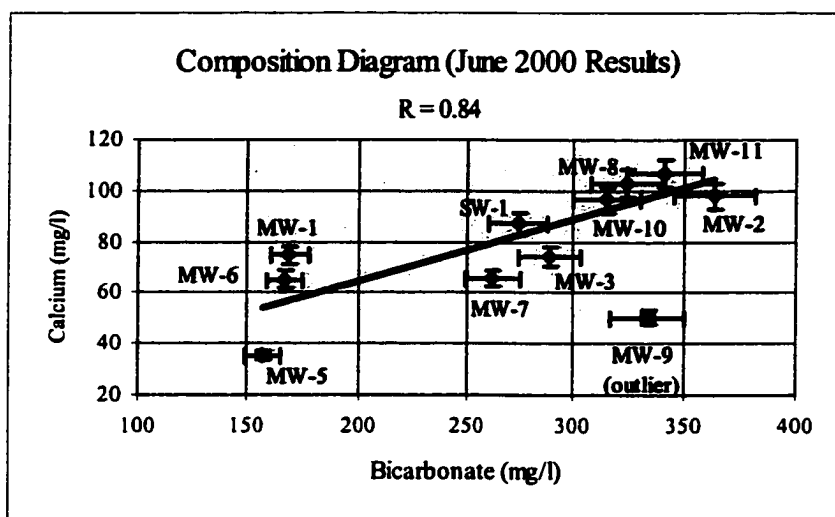


Figure 26. Calcium and Bicarbonate with $\pm 5\%$ Precision Error.

Concerning the most evident spatial trends for monitoring wells, bicarbonate concentration values increased significantly and consistently from MW-8 upgradient to MW-9 downgradient. Temporally, the only trend was a high bicarbonate concentration value for the majority of monitoring wells and Nottawa Creek surface water for December 2000.

The bicarbonate concentration values for tile drains varied from an average of 123 mg/L for TD-1 to an average of 301 mg/L for TD-8. Spatially, bicarbonate concentration values for TD-8 were consistently higher than other tile drains. There were no evident trends in bicarbonate concentration values for tile drains temporally.

Liquid ammonium nitrate (urea) and sulfur added to decrease volatilization was applied to corn fields in 2000 but not 2001. For monitoring wells, MW-8 and MW-9 exhibited the most evident spatial and temporal trend for sulfate, as sulfate concentration values decreased significantly and consistently from MW-8 upgradient to MW-9 downgradient from Dec. 1999-Dec. 2000. In this case, sulfate distribution appears to be a function of sulfate reduction, with decreased sulfate and increased bicarbonate downgradient. No other temporal or spatial sulfate concentration trends from monitoring wells, tile drains, or Nottawa Creek surface water were observed due to the fertilizer application.

Based on a 1997 soil fertility test, KCl was applied to the field where MW-9 is located at a rate of 68 kg/acre of potassium. Chloride concentration values for MW-9 ranged from 16-19 mg/L over 7 sampling events. Average chloride concentration values for other monitoring wells ranged from 2 mg/L for MW-7 to 20 mg/L for MW-10 and 28 mg/L for MW-11. It is not surprising the streambed wells (MW-10 and MW-11) had the highest average chloride concentration values for monitoring wells if it is assumed there is no sink for chloride. The average chloride concentration value for Nottawa Creek surface water was 16 mg/L.

Average chloride concentration values for tile drains ranged from 7 mg/L for TD-1 to 122 mg/L for TD-8. Based on the 1997 soil fertility test, KCl was applied at a rate of 68 kg/acre of potassium to the field which drains into TD-8. Regarding spatial trends, TD-4 had the next largest chloride concentration values ranging from 28-40 mg/L over 6 sampling events.

Total Dissolved Solids and Conductivity

The dissolved solid content of water (TDS) is proportional to specific conductance (SC), or conductivity. For the sake of brevity, this discussion will refer to TDS, keeping in mind TDS may usually be approximated as 2/3 of conductivity.

MW-4, which consistently had the largest TDS values for monitoring wells, ranged from 1600 mg/L December 1999 to 4700 mg/L March 2000. TDS concentration values for monitoring wells and Nottawa Creek surface water were at their highest in March 2000 for every well except MW-5 which had its peak concentration in June 2001, and MW-10 and MW-11 which were not tested until June 2000. The spring thaw is one explanation for the March 2000 temporally consistent monitoring well high TDS concentrations. For June 2000 Nottawa Creek surface water and monitoring well results, excluding MW-4, the only major ions that TDS was correlated with were calcium (Figure 27; $R = 0.78$) and bicarbonate ($R = 0.78$). These correlations are not unusual. Calcite equilibrium calculations for June 2000 indicated the monitoring wells were oversaturated or in equilibrium with respect to calcite.

Of the tile drains, TD-8 had the largest TDS concentration values ranging from 580-890 mg/L over 6 sampling events. Average TDS concentration values for other tile drains were similar spatially and temporally, ranging from 323 mg/L for TD-6 to 417 mg/L for TD-4.

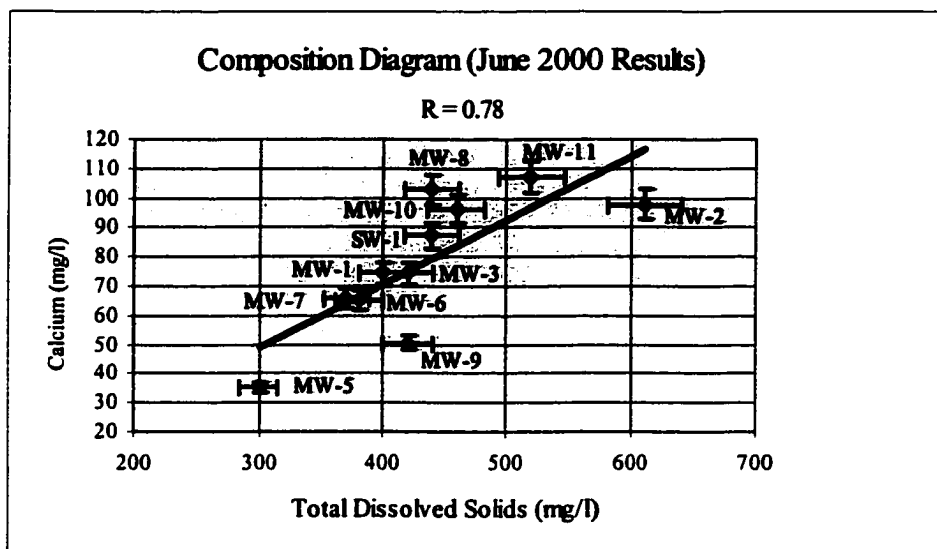


Figure 27. Scatter Diagram for Calcium and TDS with $\pm 5\%$ Precision Error.

pH

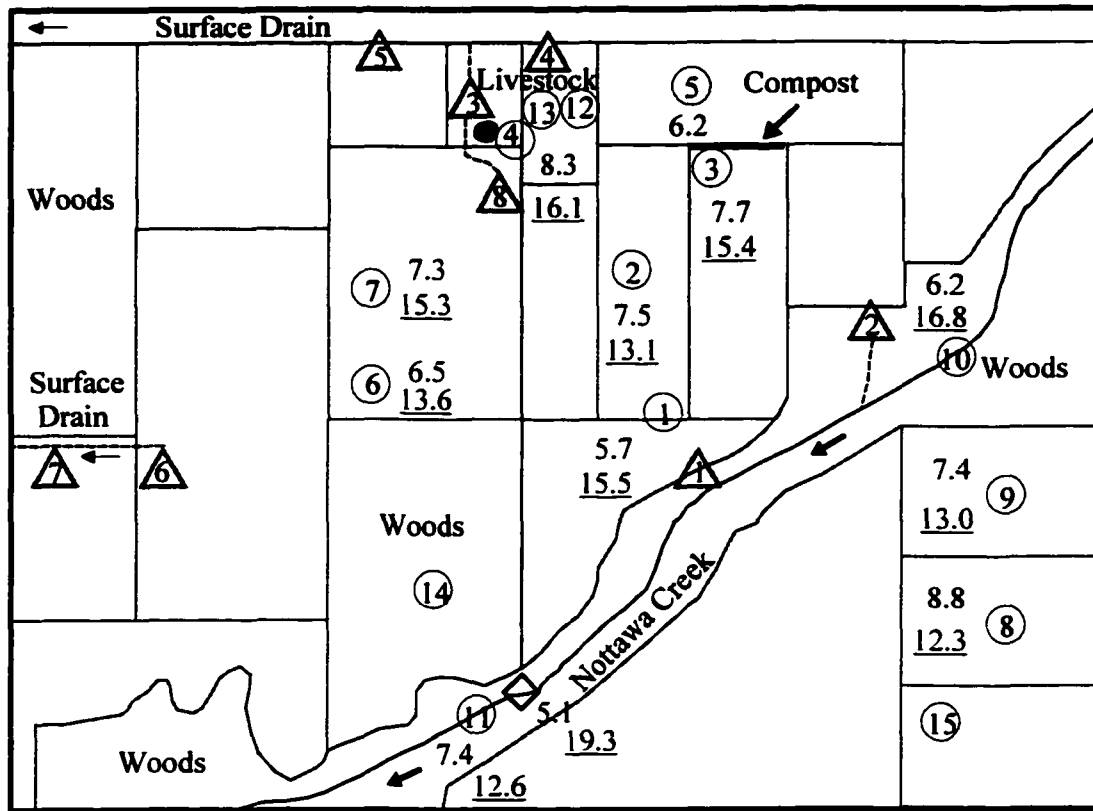
pH is defined as the negative logarithm of the hydrogen ion activity (Hounslow, 1995). Water with a pH of 7 is considered neutral, whereas below 7 is acidic and above 7 basic, respectively. The soil analysis report from 1997 stated pH of the soils tested ranged from 5.6 to 7.2 with a desired level of 6.8. The pH of monitoring well water samples for June 2001 ranged from 6.76 to 7.94. Nottawa Creek surface water pH for June 2001 measured 7.84. The pH of tile drain water samples for June 2001 ranged from 6.58 to 7.47. Changes in pH over the course of the study were relatively small. This is not unusual as dissolution of carbonate minerals in the drift buffer pH, because hydrogen ions are added to carbonate forming bicarbonate. Adding lime to the soil increases the base saturation and raises pH.

Temperature

The temperature for monitoring well water samples ranged from 4.8 °C March 2000 to 16.4 °C July 2000. Nottawa Creek surface water temperature ranged from 0.3 °C in December 2000 to 19.7 °C in June 2000. The temperature of tile drain water samples ranged from 4.5 °C in December 2000 to 20.6 °C in June 2000. Figure 28 shows monitoring well temporal and spatial variations in temperature for March and September 2001, respectively.

Phosphorus

Inorganic orthophosphate ions are the form of P utilized for uptake by plants (Manahan, 1993). Orthophosphate concentration values for the study ranged from non-detect to 0.04 mg/L with one reported abnormally high concentration value of 0.23 mg/L. P does not have a drinking water standard but the EPA recommends that Total P should not exceed 0.1 mg/L in a stream because P is the limiting nutrient for fresh water (USGS, 1999). Total P statistics for monitoring wells are shown in Table 14. Total P levels in wells were somewhat elevated, yet the two streambed wells were low for the most part. P is not considered to be very mobile, because of sorption and precipitation, and is most available to plants at neutral pH. Water samples collected for Total P were not field filtered, and P sorption to soil particles and colloids may account for the relatively high concentrations detected in monitoring



EXPLANATION

0 610 m

↑ N

▲ Tile drain outlet

● Lagoon

◇ Stream sampling site

① Monitoring well

5.7 March 2001 MW temperature in degrees Celsius

15.5 September 2001 MW temperature in degrees Celsius

Figure 28. September and March 2001 Variations in Monitoring Well Temperature.

wells. The low permeability wells had the highest Total P concentration values.

Regarding manure fertilizer, the goal was to chisel plow the equivalent of 73 kg of phosphate per acre.

Table 14

Total P Monitoring Well Statistics (mg/L)

Total P	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11
#	12	12	12	12	11	11	12	12	12	9	9
Avg.	0.49	0.23	0.10	0.06	0.14	0.05	0.18	0.04	0.08	0.08	0.03
Median	0.17	0.28	0.05	0.05	0.18	0.05	0.16	0.03	0.06	0.07	0.02
Max	1.9	0.45	0.34	0.13	0.26	0.08	0.40	0.10	0.31	0.22	0.09
Min	0.03	0.02	x	0.02	0.02	0.03	0.02	0.01	0.03	0.01	0.01
St. Dev.	0.65	0.14	0.11	0.04	0.09	0.02	0.14	0.03	0.08	0.07	0.02

x = below detection limits

Total P statistics for tile drains and Nottawa Creek surface water are shown in Table 15. Tile drains 3, 4, and 6 were at times a significant source of P to surface water yet Nottawa Creek Total P concentrations were on the average low. Maximum Total P concentrations were detected in March and May 2000, and March 2001. Total P concentration values for March dates were likely a result of spring although the May 2000 value appears to be related to a precipitation event. The maximum Total P concentration for Nottawa Creek surface water may be the result of a sampling error, as no significant precipitation had occurred for several days before sampling. Nottawa Creek surface water was always sampled mid-stream and mid-depth. The stream water level was low for that sampling period and the water pump possibly stirred up streambed sediment.

Table 15

Total P Surface Water and Tile Drain Statistics (mg/L)

Total P	SW-1	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8
#	16	11	6	7	11	7	11	9	11
Avg.	0.03	0.03	0.01	0.03	0.17	0.02	0.04	0.01	0.02
Median	0.02	0.02	0.01	0.02	0.06	0.02	0.03	0.01	0.02
Max	0.19	0.13	0.02	0.11	0.56	0.02	0.07	0.02	0.04
Min	0.01	0.01	x	x	0.02	0.01	0.02	x	0.01
St. Dev.	0.04	0.03	0.01	0.04	0.19	0.01	0.01	0.01	0.01

x = below detection limits

Total Organic Carbon

MW-4 consistently had the largest TOC values for monitoring wells and ranged from 22 mg/L to 39 mg/L. Average TOC concentration values for other monitoring wells ranged from 0.8 mg/L for MW-6 to 4.9 mg/L for MW-9. TOC concentration values for Nottawa Creek surface water ranged from 4.4 mg/L to 12 mg/L. Average TOC concentration values for tile drains ranged from 1.4 mg/L for TD-2 to 3.5 mg/L for TD-4. A comparison was made between TOC and DOC (dissolved organic carbon) concentration values for three samples only over the course of the study. The DOC and TOC values lie within the following ranges: MW-10 \pm 23%, SW-1 \pm 1.6%, and TD-4 \pm 0%. DOC samples were field filtered whereas TOC samples were unfiltered. The 0.45- μ m filter excludes almost all bacteria (Drever, 1997). DOC concentrations in groundwater not affected by pollution are generally below 2 mg/L whereas the normal range for rivers not draining wetlands or

swamps is about 4 to 6 mg/L (Drever, 1997).

Dissolved Oxygen

Maximum, average, and minimum DO concentrations for monitoring wells and Nottawa Creek surface water are shown in Figure 29. There were nine to ten

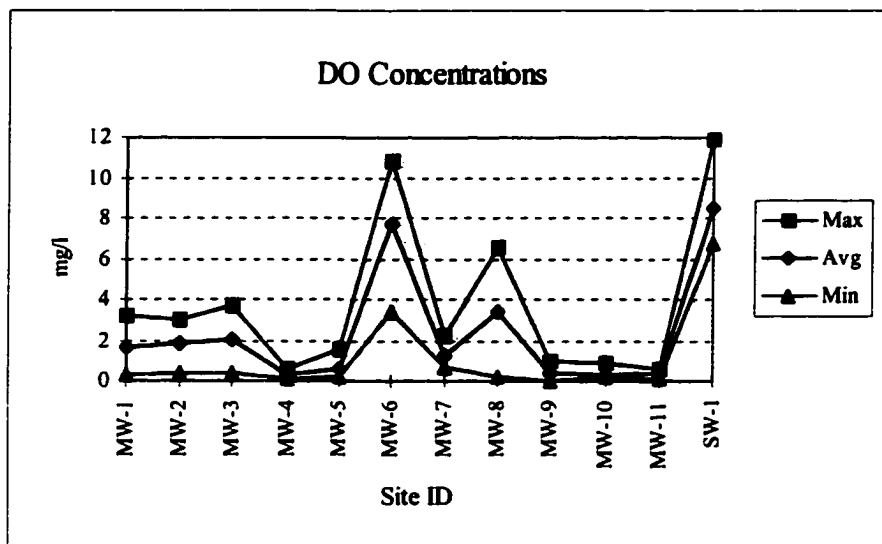


Figure 29. Spatial and Temporal DO Concentrations from May 2000 to September 2001.

readings for each site for the sampling period from May 2000 to September 2001.

Highest concentrations were in December 2000 with no pattern for lowest concentrations. Reported DO concentration values are not unusual in that DO may range in concentration from greater than 12 mg/L in a cold, flowing stream to 0 in groundwater where oxygen has been consumed by microbial decomposition of

organic matter (Drever, 1997; Hounslow, 1995).

Nitrogen

In the study area, a general nutrient objective of 68 kg of available N fertilizer per acre for corn is desired (Bob Battel, MSU Extension, personal comm., 2000). The farm accomplishes this goal through application of liquid manure, compost, and synthetic fertilizer. For liquid manure and compost most N is in the form of organic N and to be available for plant use must generally be hydrolyzed to NH_4^+ and oxidized to NO_3^- by microbial activity. In fact, NH_4^+ -N of dry matter from liquid manure was reported as 2.9 % while NH_4^+ -N of dry matter from compost was noted as 0.04 % (University of Wisconsin Soil and Forage Analysis Laboratory, 2000). Applications of liquid manure and compost together provide approximately 23 kg of N/acre. The N deficit is made up by synthetic fertilizer application. Synthetic nitrogen fertilizer practices varied from 2000 to 2001. Liquid ammonium-nitrate was applied as a side-dressing for corn in 2000 while dry urea was disked into the soil in 2001 as a spring pre-plant.

MW-4 consistently had the largest nitrate-N values for monitoring well water samples, ranging from 50 mg/L to 170 mg/L. Maximum, average, and minimum nitrate-N concentrations for monitoring wells other than MW-4 are shown in Figure 30. Nitrate-N concentrations in wells varied spatially considerably but the two streambed wells were consistently low because of mildly reducing conditions,

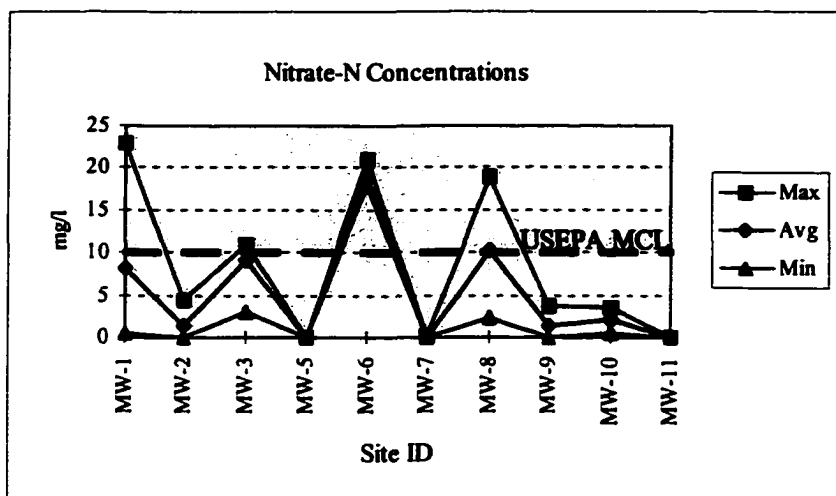


Figure 30. Nitrate-N Concentrations for Monitoring Wells.

as can be noted by anaerobic groundwater (see Figure 29). Temporally, lowest monitoring well nitrate-N concentrations were observed for December 1999. These generally low values may be attributable to the unseasonably dry fall (see Figure 18). Highest monitoring well nitrate-N concentrations were generally in June and July for 2000 and 2001, coinciding with recent fertilizer applications. However, some wells exhibited no clear pattern for peak concentrations.

Overall, nitrate-N concentration values for wells in soybean fields were significantly lower as compared to wells in corn fields. Soybeans are legumes and do not require applied N fertilizer as bacteria on their root structures are capable of fixing atmospheric nitrogen (Manahan, 1993).

Three out of the four private wells sampled for the dissertation study tested above the MCL for nitrate as nitrogen (MW-12, MW-13, and MW-15). The private well sampled during the study that was not contaminated with nitrate (MW-14) had

the well screen set at a depth between 10 and 12 m. This relatively shallow well was protected by a 30 cm clay layer above the well screen. In addition, the residence was surrounded by woods, which could help lower the redox potential for groundwater.

Maximum, average, and minimum nitrate-N concentrations for tile drains and Nottawa Creek surface water are shown in Figure 31. TD-1 consistently had the

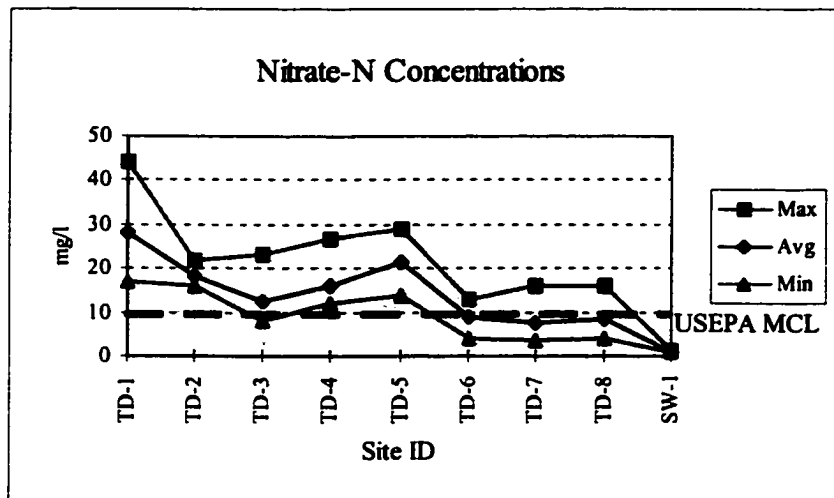


Figure 31. Nitrate-N Concentrations for Tile Drains and Nottawa Creek.

largest nitrate-N values (26.6 mg/L average) for tile drain water samples while TD-7, a short single tile run, had the lowest (7.4 mg/L average). Although nitrate-N concentrations in tile drains were relatively high, Nottawa Creek surface water was consistently low with a maximum value of 1.3 mg/L, a minimum value of 0.71 mg/L, and an average value of 0.97 mg/L. A clear pattern was observed temporally and spatially for lower nitrate-N concentration values for tiles draining soybean fields as compared to higher nitrate-N concentration values for tiles draining corn fields.

Selected nitrate-N concentration values for MW-1, MW-2, TD-1, and TD-2 are listed for comparison in Table 16 and Figure 32. These values show how nitrate-

Table 16

Nitrate-N Concentration Values for Wells and Tile Drains Located in Fields Planted in Corn (2000) and Soybeans (2001)

	MW-1	MW-2	TD-1	TD-2
March 2000	9.9	0.06	25	---
March 2001	1.80	4.4	21	17
May 2000	0.47	0.29	41	20
May 2001	3.7	3.8	20	17
June 2000	21	0.11	44	22
June 2001	0.75	3.7	17	18
July 2000	23	0.23	43	---
July 2001	2.7	2.4	20	16
Fall 2000	10	0.07	26	---
Fall 2001	13	1.15	10	---

--- no sample (tile drain not flowing)

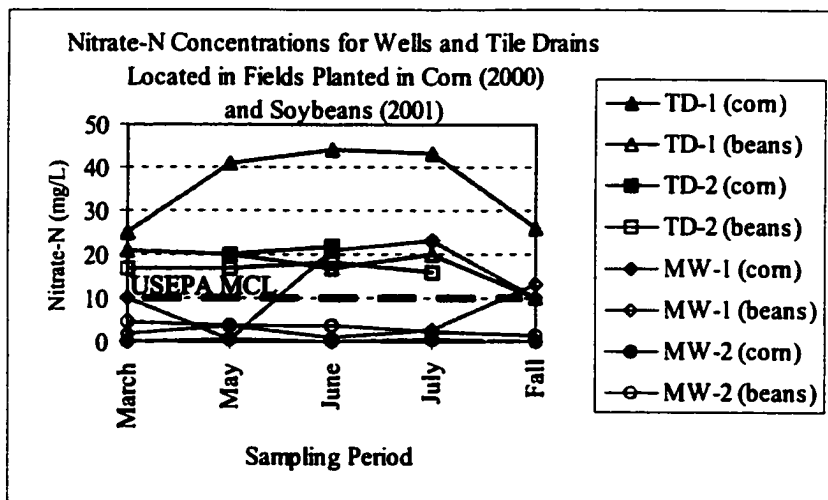


Figure 32. Nitrate-N Concentration Values for Sites in Corn and Soybeans.

N concentration values varied with crop management (see Figures 9 and 10). Nitrate-N concentration values for wells and tile drains were significantly higher in 2000 when corn was grown versus 2001 when soybeans were planted. MW-2 nitrate-N concentration values were comparatively low for both years because of fluctuating aerobic to anaerobic groundwater.

MW-4 consistently had the largest $\text{NH}_3\text{-N}$ values for monitoring wells and ranged from 4 mg/L to 31 mg/L. A sample of the lagoon surface water was reported as 770 mg/L as $\text{NH}_3\text{-N}$ while nitrate-N concentration was non-detect. Other monitoring wells ranged from non-detect to 0.2 mg/L for MW-9. $\text{NH}_3\text{-N}$ concentration values for Nottawa Creek surface water ranged from 0.02 mg/L to 0.09 mg/L. These values were below the USEPA freshwater aquatic life chronic criteria based on total ammonia as nitrogen, which is dependent on pH and temperature (see <http://www.epa.gov/ost/standards/ammonia>). $\text{NH}_3\text{-N}$ concentration values for tile drains were non-detect for all drains except TD-4 and TD-6. $\text{NH}_3\text{-N}$ average concentration values for TD-4 were 0.5 mg/L and 0.2 mg/L for TD-6.

Iron

It is assumed that soluble iron concentrations reported here represent the ferrous ion (Fe^{+2}) since the ferric (Fe^{+3}) ion is the oxidized form and has very low solubility. In addition, since metals were field filtered, ferric iron oxide present on aquifer mineral grains would not be expected to be present in water samples.

Dissolved iron concentrations were detected in every monitoring well for at least two sampling events with MW-5 and MW-7 having three detections while soluble iron was detected each of the eight sampling events for MW-9 and Nottawa Creek surface water. Soluble iron was detected each of the six sampling events for MW-10 and MW-11. Most wells with two to three detections were confined to the relatively low static water level period of December 1999 and March 2000 and ranged from 0.1 mg/L to 1.8 mg/L of dissolved iron. Soluble iron average concentration values were 2.57 mg/L for MW-9, 0.70 mg/L for MW-10, and 3.52 mg/L for MW-11. The consistent detection of soluble iron for MW-10 and MW-11 suggest redox potential is lower in discharge areas, which means nitrate is unlikely to be present in high concentrations. Visually, iron staining of Nottawa Creek banks and streambed during stream low flow stages again reinforce the supposition baseflow is a major component of total stream flow. Soluble iron concentration values for Nottawa Creek surface water ranged from 0.01 mg/L to 0.18 mg/L. Tile drain soluble iron concentration values were non-detect for all drains except TD-3 and TD-4. Soluble iron was detected once for TD-3 at a value of 0.02 mg/L in September 2000. Soluble iron was detected five out of the six metal sampling events for TD-4 with concentration values ranging from 0.027 mg/L to 0.12 mg/L.

Evaluating Shallow Groundwater Vulnerability with Environmental Isotopes

Water samples from the June and September 2001 sampling events were

collected for δD , $\delta^{18}O$, and $\delta^{13}C_{DIC}$ analysis. A table of values for δD , $\delta^{18}O$, and $\delta^{13}C_{DIC}$ results are shown in Table 17. Very enriched δD and $\delta^{18}O$ values for MW-4 are noteworthy in that they signify evaporation from the lagoon prior to recharge.

Graphs of precipitation data and ground water levels for the June and September 2001 sampling periods are shown in Figures 33 and 34. Sampling

Table 17

H, O, and C Stable Isotope Results from June and September 2001

Sample	June	September	June	September	June	September
	$\delta D(\text{‰})$	$\delta D(\text{‰})$	$\delta^{18}O(\text{‰})$	$\delta^{18}O(\text{‰})$	$\delta^{13}C(\text{‰})$	$\delta^{13}C(\text{‰})$
MW-1	-56.53	---	-8.19	-8.9	-11.75	-13.6
MW-2	-53.07	---	-7.49	-8.9	-11.43	-10.5
MW-3	-52.86	---	-7.87	-8.9	-11.01	-10.8
MW-4	-47.99	---	-6.47	-7.9	-10.83	-11.6
MW-5	-55.05	---	-8.39	---	-12.03	---
MW-6	-57.38	---	-7.64	-8.8	-8.86	-12.4
MW-7	-61.80	---	-8.47	-9.3	-12.53	-12.3
MW-8	-57.58	---	-7.71	-8.9	-11.10	-11.2
MW-9	-52.55	---	-7.86	-9.3	-12.71	-12.7
MW-10	-60.29	---	-7.78	-9.0	-10.66	-10.9
MW-11	-62.79	---	-8.17	-9.1	-12.35	-12.5
MW-12	-56.42	---	-6.89	-8.8	-12.28	-12.9
MW-13	-58.03	---	-8.60	-8.8	-11.40	-11.9
MW-14	-53.04	---	-7.49	-9.2	-13.77	-13.2
MW-15	-54.42	---	-7.85	-8.9	-11.71	-10.8
SW-1	-59.78	---	-7.11	-8.6	-12.22	-11.9
TD-1	-66.36	---	-8.17	-8.1	-9.48	-13.3
TD-2	-66.64	---	-8.80	---	-8.79	---
TD-4	-62.24	---	-8.04	-7.2	-10.69	-13.9
TD-6	-64.09	---	-8.58	-9.2	-14.67	-11.4
TD-7	-57.69	---	-8.19	---	-9.02	---
TD-8	-66.11	---	-8.29	-9.0	-10.47	-9.8

--- no measurement

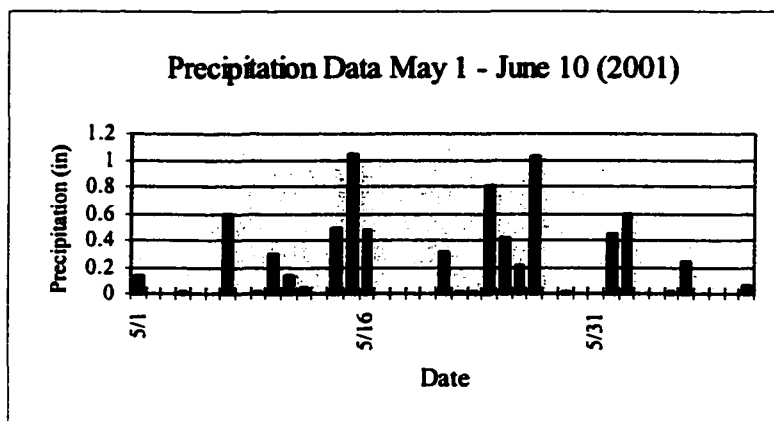


Figure 33. Precipitation Data for the June 2001 Sampling Event.

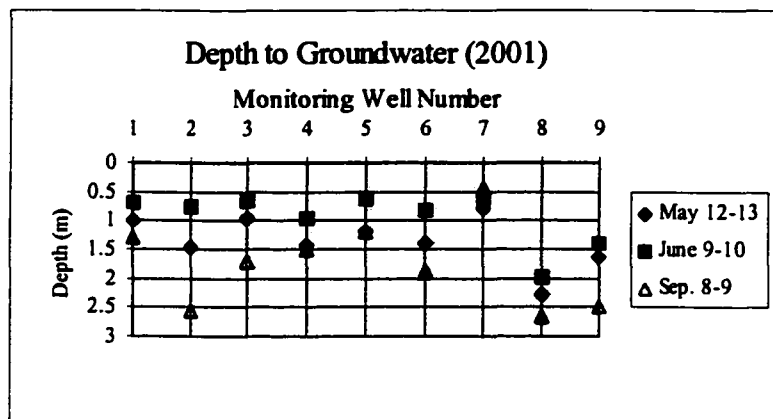


Figure 34. Monitoring Well Groundwater Levels for May, June, and September 2001.

occurred June 9th and 10th. There was substantial rainfall on June 1st and 2nd with a lesser amount on June 6th. Groundwater levels were actually significantly higher in June than May, and relatively low in September, as it had not rained for two weeks prior to sampling. It rained approximately 5 cm from September 7th through the 9th. A scatter diagram of δD and $\delta^{18}O$ results for monitoring wells and Nottawa Creek

surface water from June 2001 are shown in Figure 35. Since the wells are relatively shallow, it may be assumed precipitation events strongly influence the isotopic composition of recharge. Three year averages of $\delta^{18}\text{O}$ precipitation values from the Kalamazoo, Michigan area are approximately -9‰ for September through November, -15‰ for December through March, and -6‰ for April through August (Kehew et al., 1999a). The average $\delta^{18}\text{O}$ value for the monitoring wells above (excluding MW-4) is -7.9‰. This value suggests there is significant mixing between summer precipitation and the winter snow melt in the vadose zone before recharge. Machavaram and Krishnamurthy, 1995) cite weighted average δD precipitation values from the Kalamazoo area as -30‰ for summer (June-October) and -100‰ for winter

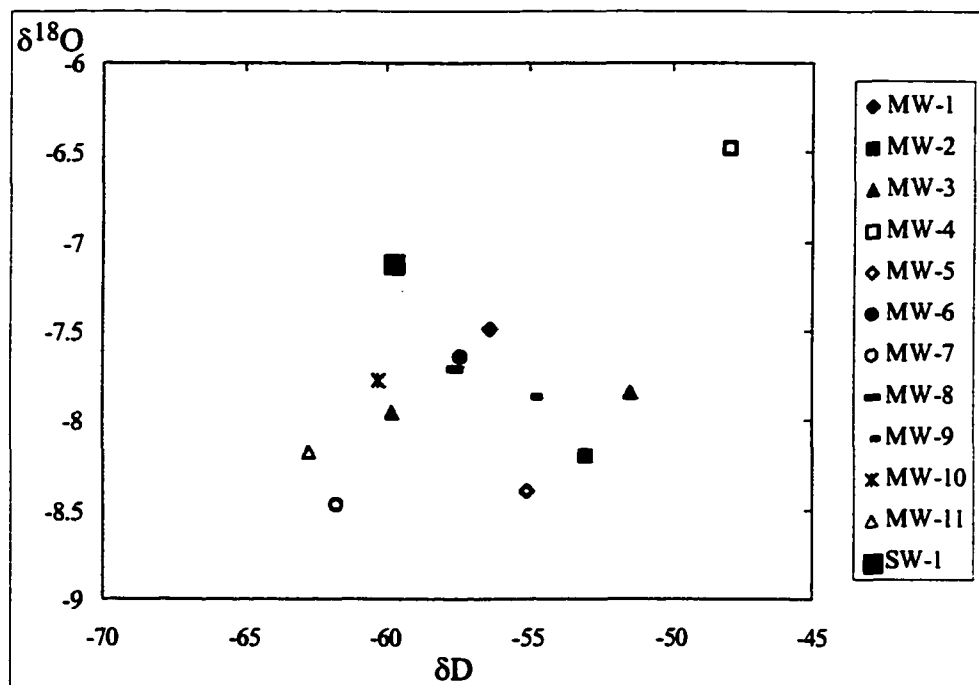


Figure 35. A Scatter Diagram of Monitoring Well and Nottawa Creek Surface Water δD and $\delta^{18}\text{O}$ Results from June 2001.

(November-February). The average δD value for the monitoring wells above (excluding MW-4) is -56‰. This value also suggests there is some mixing within the waters recharging the aquifers between summer precipitation and the isotopically light winter precipitation. Enrichment in $\delta^{18}O$ for Nottawa Creek surface water is very pronounced, as the lighter O isotope preferentially evaporates. The average $\delta^{18}O$ value for groundwater in southwest Michigan is approximately -10‰ (Kehew et al., 1999a). The data above suggest most monitoring wells respond very quickly to recharge events.

$\delta^{18}O$ results for monitoring wells and Nottawa Creek surface water from June and September 2001 are shown in Figure 36. The September values are more depleted than the June values. This may suggest more isotopically homogenous

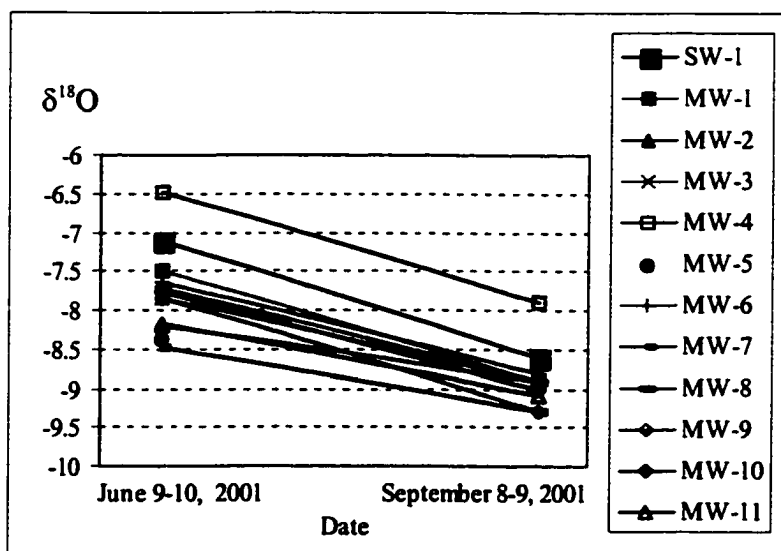


Figure 36. A Scatter Diagram of Monitoring Well and Nottawa Creek Surface Water $\delta^{18}O$ Results from June and September 2001.

recharge waters because there had not been any precipitation for two weeks prior to September 7, when it rained 0.64 cm. On September 8 it rained 1.9 cm and on September 9 it rained 2.4 cm. The average $\delta^{18}\text{O}$ value for September monitoring wells of -9.0‰ (excluding MW-4) is closer than the June average of -7.9‰ to the average $\delta^{18}\text{O}$ value for groundwater in southwest Michigan of approximately -10‰.

δD and $\delta^{18}\text{O}$ results for tile drains and Nottawa Creek surface water from June 2001 are shown in Figure 37. Enrichment in δD for Nottawa Creek surface water is

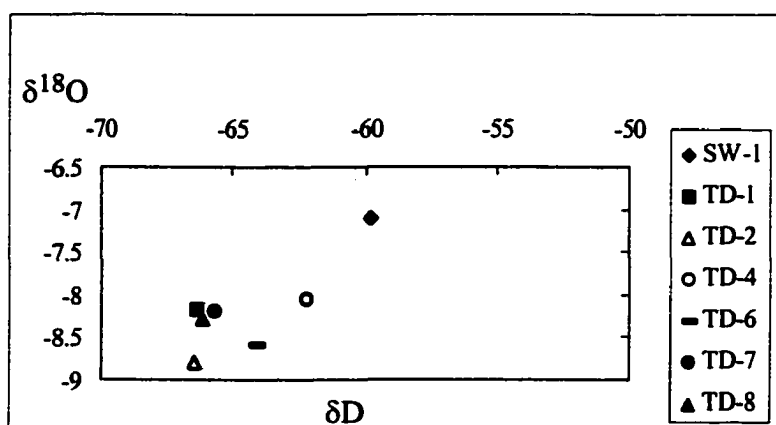


Figure 37. A Scatter Diagram of Tile Drain and Nottawa Creek Surface Water δD and $\delta^{18}\text{O}$ Results from June 2001.

pronounced, as the lighter ^1H and ^{16}O isotopes preferentially evaporate. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data for the tile drains is even more pronounced than for monitoring wells. The average $\delta^{18}\text{O}$ value for the tile drains is -8.3‰ whereas the average δD value is -65‰. These values are somewhat surprising because the average values are more depleted than the monitoring well average values of -7.9‰ for $\delta^{18}\text{O}$ and -56‰ for δD . There is

usually a small isotopic enrichment during the summer, particularly near the surface, because of evaporation. The δD and $\delta^{18}O$ values suggests there is significant mixing between summer precipitation and the winter snow melt in soil water before recharge. The isotopic ratios still suggest most tile drains respond quickly to infiltration events. Field observations support this notion.

δD and $\delta^{18}O$ results for tile drains and Nottawa Creek surface water from June and September 2001 are shown in Figure 38. The average $\delta^{18}O$ value for September

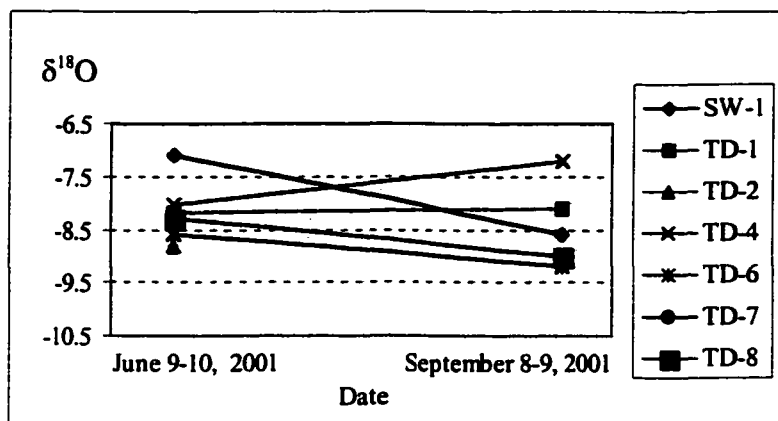


Figure 38. A Scatter Diagram of Tile Drain and Nottawa Creek Surface Water $\delta^{18}O$ Results from June and September 2001.

tile drains of -8.4‰ is nearly identical to the average $\delta^{18}O$ value for June tile drains of -8.3‰. Again the June average $\delta^{18}O$ value is somewhat surprising because it is more depleted in ^{18}O than the monitoring well average of -7.9‰. The average $\delta^{18}O$ value for September tile drains of -8.4‰ is intuitively closer in line to what one may suspect compared to the average $\delta^{18}O$ September monitoring well value of -9.0‰,

because of some evaporation near the surface and thus a small isotopic enrichment.

Alkalinity as HCO_3^- vs. $\delta^{13}\text{C}_{\text{DIC}}$ results from June 2001 are plotted in Figure 39 for monitoring wells. It may be noted from the correlation coefficient that the sign is

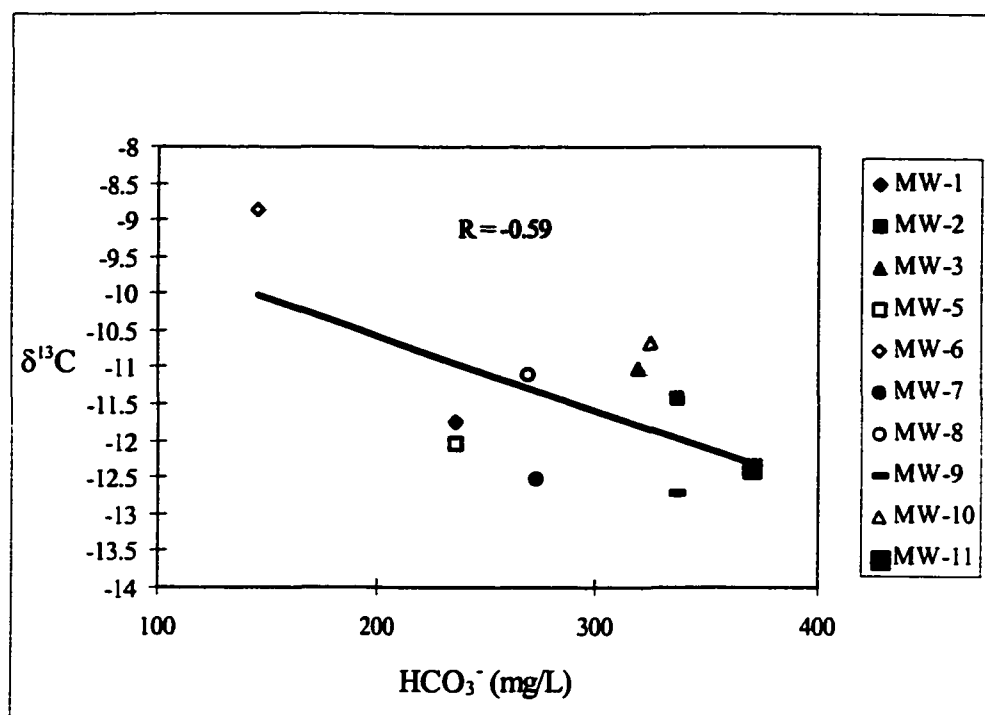


Figure 39. $\delta^{13}\text{C}_{\text{DIC}}$ vs. Alkalinity Monitoring Well Results from June 2001.

(-) and the value not high enough for a strong correlation between alkalinity and $\delta^{13}\text{C}_{\text{DIC}}$ values. The significant variation of alkalinity and $\delta^{13}\text{C}_{\text{DIC}}$ values between wells suggests carbonate dissolution pathways and/or redox conditions vary throughout the study area. For example, calcite equilibrium modeling for June suggested MW-5 was oversaturated with respect to calcite. More negative $\delta^{13}\text{C}_{\text{DIC}}$ values can imply denitrification because the $\delta^{13}\text{C}$ values of soil organic carbon, which

is utilized for denitrification, is more negative than $\delta^{13}\text{C}$ alkalinity values from inorganic carbon (Nascimento et al., 1997). This assumption used in conjunction with relative increases in bicarbonate concentrations may be an indicator of denitrification, because bicarbonate may also be a by-product of denitrification (Korom, 1992). In fact, wells plotted at either end of the regression line support these notions. MW-11 had non-detect concentrations of nitrate and low DO concentrations whereas MW-6 had a nitrate concentration of 21 mg/L and a DO concentration of 10.2 mg/L. The observations above are generalizations because the dominant type of vegetation establish the initial $\delta^{13}\text{C}$ values of soil organic carbon, and in turn may be modified by diffusion of carbon dioxide from the vadose zone (Nascimento et al., 1997).

The $\delta^{13}\text{C}_{\text{DIC}}$ values for monitoring wells from June and September 2001 are shown in Figure 40. Based on a previous study, the $\delta^{13}\text{C}_{\text{DIC}}$ in isotopic and chemical equilibrium with respect to carbonate is expected be around -12‰ (Nascimento et al., 1997). If diffusion to the atmosphere is significant, the $\delta^{13}\text{C}$ of DIC would be approximately -9‰. The June $\delta^{13}\text{C}_{\text{DIC}}$ result for MW-6 of approximately -9‰ suggests diffusion to the atmosphere may be significant. MW-6 was located in a field planted in corn but had previously been fallow since wheat was harvested July 2000. Because there is no significant correlation between alkalinity and $\delta^{13}\text{C}_{\text{DIC}}$ (see Figure 37), it may indicate most waters travel through the vadose zone fairly quickly. In fact, while the June results were negatively correlated ($R=-0.59$), the September results were positively correlated ($R = 0.51$).

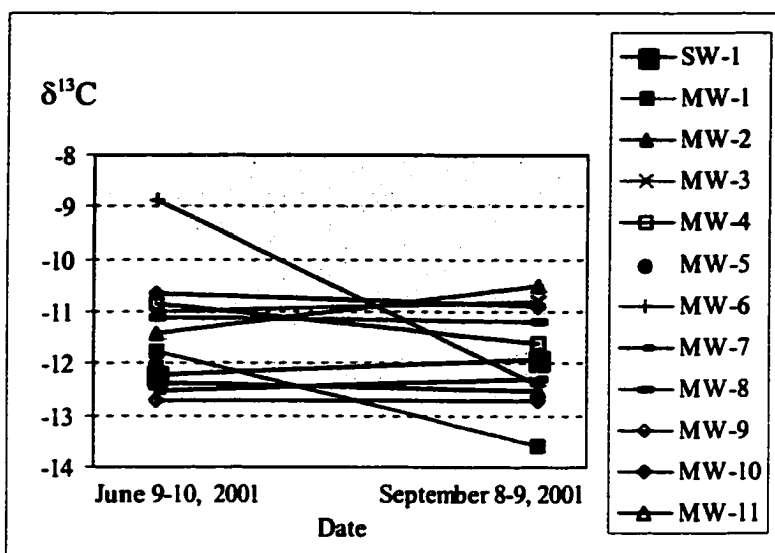


Figure 40. Monitoring Well $\delta^{13}\text{C}_{\text{DIC}}$ Values from June and September 2001.

The $\delta^{13}\text{C}_{\text{DIC}}$ values for tile drains and Nottawa Creek surface water from June and September 2001 are shown in Figure 41. The June $\delta^{13}\text{C}_{\text{DIC}}$ result for TD-2, TD-7, and TD-1 of approximately -9‰ suggests diffusion to the atmosphere to be significant.

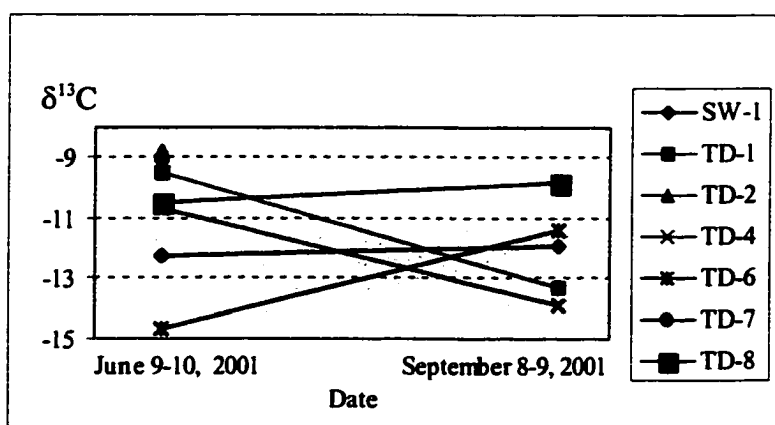


Figure 41. Tile Drain and Nottawa Creek Surface Water $\delta^{13}\text{C}_{\text{DIC}}$ Values from June and September 2001.

The correlation coefficient for alkalinity as HCO_3^- vs. $\delta^{13}\text{C}_{\text{DIC}}$ for tile drains was -0.22 for June and 0.80 for September 2001. These results likewise indicate dissolution does not follow the usual open or closed pathway. Regarding aquifer vulnerability, infiltrating water may reach the tiles quickly after leaving the soil zone. In fact, tile drains have been shown to be a major contributor of contaminants to surface water.

Samples were collected for T analysis from the two streambed wells only for the September 2000 sampling event. The results in TU for MW-10 was 10.6 ± 0.8 while the TU value for MW-11 was 10.2 ± 0.9 thus indicating groundwater discharging into Nottawa Creek is post-bomb water. This indicates the possibility that contaminants may be transported along the groundwater flow path from recharge areas within the watershed and discharged into Nottawa Creek surface water.

Tracing Nitrogen Sources with Isotope Fractionation of Nitrate-Nitrogen and Nitrate-Oxygen

This study assesses the fate of applied nitrogen by source availability and type utilizing the stable isotope ratios $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of NO_3^- as a geochemical tracer. A general nutrient objective of 68 kg of available N fertilizer per acre for corn is accomplished through application of liquid manure, compost, and synthetic fertilizer. Laboratory analysis of liquid manure and compost report applications at the rate applied provided approximately 23 kg N/acre. For the 2000 growing season, the N

deficit for corn was made up through application of liquid ammonium-nitrate as a side-dressing.

Twelve samples were collected for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ from various sampling events. A table of values for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ results is shown in Table 18. These values are plotted on Figure 42 along with typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from various sources.

The $\delta^{15}\text{N}$ 13.55‰ value for compost lies within the range of animal manure. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values for MW-3, the well adjacent to the compost pile, lie within the overlapping isotopic signature range of manure and denitrification. The MW-3 DO concentration value for June was 1.51 mg/l, whereas the DO concentration value for Oct. was 0.64 mg/l. The low DO concentration for October, along with $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ enrichment relative to the June isotopic signature may indicate denitrification. The high DO concentration value for June, along with similarity to the isotopic signature for compost seems to imply lack of denitrification. However, because water samples were not obtained at specific depth intervals there is a possibility of mixing between waters of varying redox potential.

MW-4, the well adjacent to the animal waste lagoon, exhibits a denitrification isotopic signature with $\delta^{15}\text{N}$ values over 28‰ for both sampling dates. The DO concentration value for June was 0.1 mg/l while the DO concentration value for October was 0.14 mg/l. MW-4, besides having a concentration a high concentration of nitrate, also had an ammonia concentration of 23 mg/L. In June of 2000, the lagoon was sampled and tested for ammonia and nitrate, yielding a value of 770 mg/L

Table 18

 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of Nitrate Results

Date	ID	$\delta^{15}\text{N}$ air	$\delta^{18}\text{O}$ VSMOW	$\text{NO}_3\text{-N}$ (mg/L)	DO (mg/L)
6-17-00	TD-1	5.84	3.1	44	
6-17-00	MW-3	13.78	6.7	9.3	1.51
6-17-00	MW-4	28.62	10.6	170	0.10
6-17-00	MW-6	5.81	4.0	18	5.49
7-15-00	MW-1	7.4	4.2	23	1.51
7-15-00	TD-1	5.8	3.1	43	
10-01-00	MW-3	17.0	8.16	9.5	0.64
10-01-00	MW-4	28.65	10.26	120	0.14
10-01-00	MW-6	6.3	3.34	18	6.78
10-01-00	MW-8	3.1	1.87	15	6.32
10-01-00	Compost*	13.55			
12-10-00	Synthetic*	-0.36			

* Result includes ammonia, dissolved organic nitrogen, and nitrate

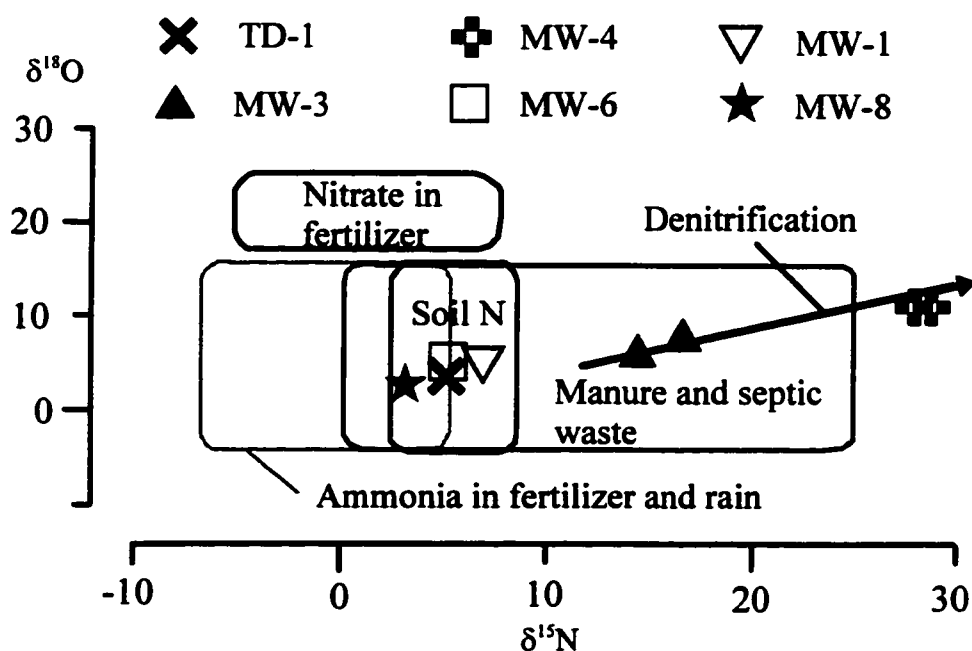


Figure 42. $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ Results with Typical Ranges from Various Sources (After U.S. Geological Survey, 2000).

as $\text{NH}_3\text{-N}$, and no detectable nitrate.

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ results for TD-1, MW-1, and MW-6 lie within overlapping value ranges of NH_3 in fertilizer and rain, soil N, and manure and septic waste. However, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values for these results are clearly centered within the isotopic signature range of soil N.

The $\delta^{15}\text{N}$ result for MW-8 of 3.1‰ and $\delta^{18}\text{O}$ value of 1.87‰ is within the range of overlapping values for NH_3 in fertilizer and rain, soil N, and manure and septic waste. However, the value is near the fringe of the soil N range. The $\delta^{15}\text{N}$ value of -0.36‰ for the liquid ammonium-nitrate tested lies within the range for synthetic fertilizer. The result for MW-8 would seem to indicate a possible synthetic fertilizer source versus compost because the compost isotopic signature was 13.55‰. Unfortunately, the EIL was unable to test the submitted synthetic fertilizer for $\delta^{18}\text{O}$, which may have helped provide enough isotopic contrast to make a definitive interpretation. For example, Aravena et al. (1993) report synthetic fertilizers are characterized by $\delta^{18}\text{O}$ values of 18 to 22‰. However, in this case, a mixture of ammonium-nitrate fertilizer suggests a possibly lesser value.

Sediment Grain Size Analysis and in Situ Denitrification Potential

Forty sediment samples collected from monitoring well borings were analyzed to investigate possible links between aquifer nitrate concentrations and grain size. These samples represent soil profile grain sizes from surface samples through the

saturated zone. This research was partially initiated because of large spatial variation in nitrate concentrations between wells. Two pairs of wells were especially noteworthy, considering their nominal distance apart of 150 horizontal meters. For one of the pairs of wells, MW-6 had average nitrate-N concentration values of 19 mg/l while MW-7 had average nitrate-N concentration values of 0.06 mg/l. As discussed previously, MW-6 and MW-7 are apparently separated by a groundwater divide. For the other pair of wells, MW-8 (upgradient) had average nitrate-N concentration values of 9.9 mg/l while MW-9 (downgradient) had average nitrate-N concentration values of 1.2 mg/l.

All forty sediment samples were analyzed for grain size by mechanical sieving and the hydrometer method. For the sake of brevity, an example of the results for one sample are displayed. The following three graphs refer to sample 5 from MW-5 (see Appendix A).

Figure 43 is a graph of hydrometer results utilized to estimate percentages of silt and clay. After sieving, only the fine-grain portion of the sample was used for the hydrometer analysis. For example, for the given sample, 50 grams of a silt and clay mixture were used from a sieve analysis. The Wentworth grain size scale is adhered to in this study. The percent of clay in the sample was taken from the graph at $x = 0.004$ mm. This percentage was then multiplied by the total weight of fines to determine the weight of clay. In this instance, 32% as clay times the total fines of 79.55 grams equals 25.46 grams. This value was then converted to a percentage of the total sieved sample. For example, $(25.46/426.42)$ times 100 equals 6.0%.

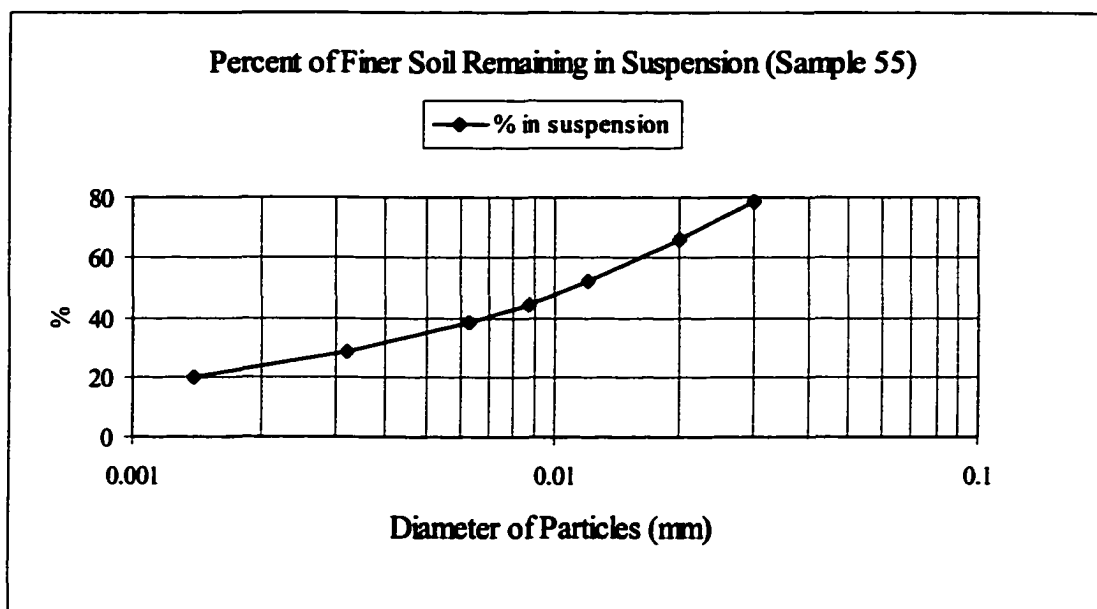


Figure 43. A Hydrometer Graphing Result for Sample Number 55.

Figure 44 is a histogram of grain sizes. In sum, this sample was described as a gray, poorly sorted, silty medium to fine sand with 6.0% clay. Gravel was predominantly of granule size with some pebbles for all samples. Sieves were not employed to separate gravel.

A cumulative frequency curve is displayed in Figure 45 which allows one to calculate quantitatively the degree of sorting. The following inclusive graphic standard deviation equation and descriptions were adopted (McLane, 1995):

$$(\phi_{84} + \phi_{16})/4 + (\phi_{95} - \phi_5)/6.6$$

<0.35 ϕ	Very well sorted
0.35 ϕ -0.50 ϕ	Well sorted
0.50 ϕ -0.71 ϕ	Moderately well sorted
0.71 ϕ -1.00 ϕ	Moderately sorted
1.00 ϕ -2.00 ϕ	Poorly sorted
>2.00 ϕ	Very poorly sorted.

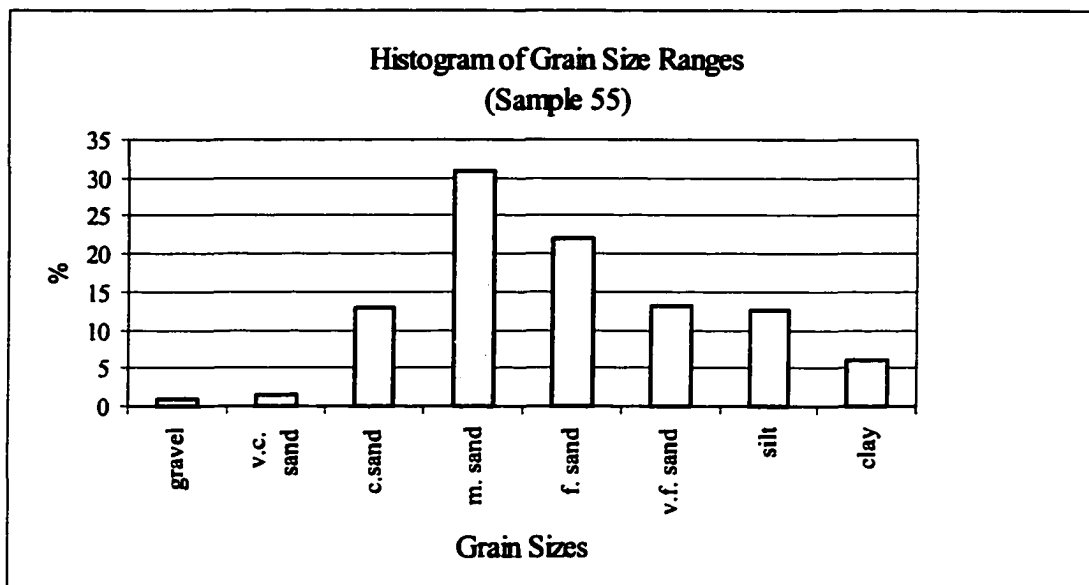


Figure 44. A Histogram Graphing Result for Sample 55.

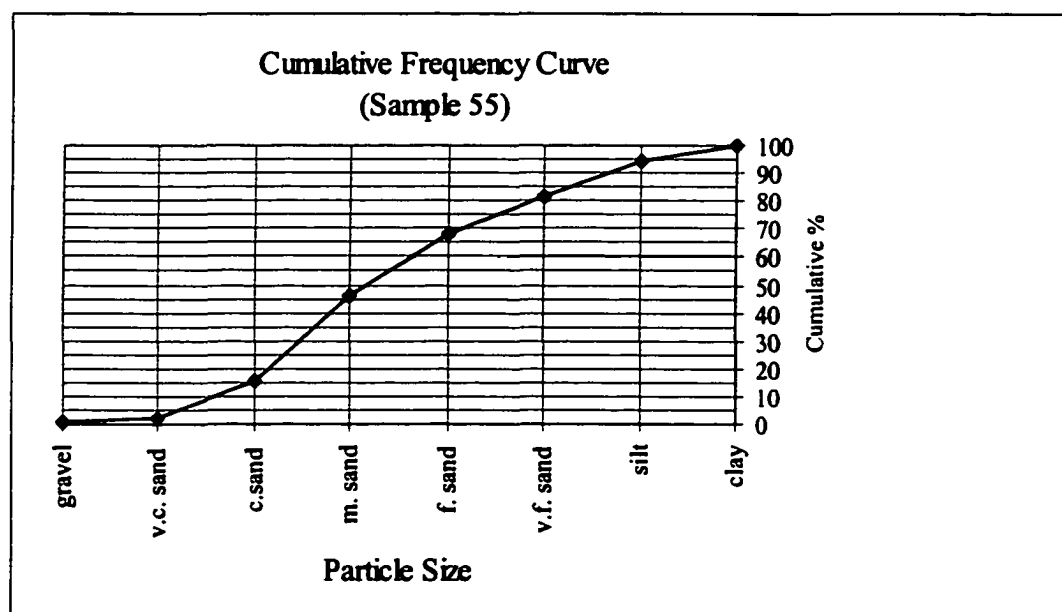


Figure 45. A Cumulative Frequency Curve Result for Sample 55.

The main limitation of grain size analysis was the collection process of soil and sediment samples. Disturbed recovery from auger drilling likely inhibited an authentic recovery of sample. On the other hand, grain size analysis provides a tremendous improvement in detail versus macroscopic description by itself.

After separation of the clay and silt fractions by the hydrometer method, several aquifer sediment samples were analyzed by XRD. Kaolinite, illite, and chlorite were identified as the primary clay minerals present.

Lithologic descriptions for samples may be described as generally ranging from medium to coarse textured (see Appendix A for detail). In regard to fine textured sediment, very little clay was detected for most samples (6 % maximum) although the vast majority of samples were classified as silty sands. The Coldwater Shale split spoon sample from MW-1 was an exception to the general classification scheme and described as a silt with 6.2 % clay.

Redox conditions were likely more influential on nitrate concentrations in groundwater than grain size, with DO, nitrate, and iron concentrations serving as indicators. Pore water chemistry parameters, for the purpose of this discussion, include DO, NO_3^- , Fe, and TOC.

The aquifer sediment sample for MW-6 was classified as a light olive brown, poorly sorted, silty fine sand, while the aquifer sediment sample for MW-7 was classified a gray, very poorly sorted, silty medium to fine sand. MW-6, with average nitrate-N concentrations of 19 mg/l, was consistently at or near saturation with DO (average 7.6 mg/l). Consequently, denitrification could not proceed since free oxygen

is the favored electron acceptor by aerobic bacteria (Kehew, 2001). In addition, average TOC concentrations were 0.8 mg/l for MW-6 indicating a suitable electron donor (reactive organic carbon) present at very low concentrations. The redox potential was lower for MW-7 with DO concentrations ranging from 0.66 to 2.29 mg/l although MW-7 also had comparatively low average TOC concentrations (1.1 mg/l). Average nitrate-N concentrations for MW-7 were 0.06 mg/l.

The aquifer sediment sample for MW-8 was classified as a yellowish brown moderately sorted, silty coarse to medium sand, while the aquifer sediment sample for MW-9 was classified a yellowish brown, moderately sorted, sandy gravel,. MW-8, over the course of the study, averaged 9.9 mg/l of nitrate-N. MW-8 average DO concentrations were 3.0 mg/l. The DO concentration was consistently above the level of 1 mg/l the redox potential must fall below for nitrate to be used as an electron acceptor (Kehew, 2001). However, average TOC concentrations of 2.2 mg/l indicate organic carbon was sufficiently present to be utilized as a electron donor. The redox potential was lower for MW-9 with DO concentrations ranging from 0.04 to 0.79 mg/l. In addition, MW-9 had comparatively high average TOC concentrations (5.1 mg/l). Nitrate-N concentrations for MW-9 ranged from 0.01 to 3.5 mg/l. The redox potential for MW-9 was in the suboxic range with Fe concentrations averaging 2.5 mg/l indicating consumption of nitrate by facultative microorganisms.

Average nitrate-N concentrations were 7.8 mg/l for MW-1, 1.4 mg/l for MW-2, and 9.0 mg/l for MW-3. The redox potential for MW-1, MW-2, and MW-3 was in the oxic range with DO concentrations above 1 mg/l over the course of the study.

The redox potential for MW-5 was also in the oxic range. However, the average DO concentration for MW-5 was 0.56 mg/l while nitrate-N concentrations averaged 0.01 mg/l. TOC concentrations averaged between 2 and 3 mg/l for MW-1, MW-2, MW-3, and MW-5. The aquifer sediment samples for these wells were classified as silty medium to fine sands.

Field Scale Evaluation of the Fate of Agrichemicals with the Immunoassay Test

Transport of herbicides is controlled by soil biological, chemical, and physical properties (Meyer and Thurman, 1996). For example, it has been suggested that atrazine has a relatively low leaching potential when soil organic matter is greater than 2% (Meyer and Thurman, 1996). However, this is under ideal conditions and obviously cannot take into account preferential flow and tile drainage (Kehew, 2001; Fenelon and Moore, 1998). A topsoil analysis report from 1997 for the farm reports soil organic matter for the various fields ranging from 1.5 to 2.5 percent, which suggests low to moderate leaching potential. Degradation of pesticides in the unsaturated zone is more likely to occur when strongly sorbed to organic carbon (Kehew, 2001).

Microbial activity is thought to play a large part in pesticide breakdown but they can also degrade by abiotic processes. For example, atrazine can degrade by chemical hydrolysis to hydroxyatrazine as a water molecule reacts to replace the chloride with the hydroxide portion of water.

The results from samples collected in June, July, and early Fall (September-October) of 2000 are listed in Table 19. The alachlor immunoassay test results

Table 19

Year 2000 Herbicide Concentrations as Detected by Alachlor and Triazine Immunoassay Tests (Concentrations in μL)

	June 2000 alachlor	June 2000 triazines	July 2000 alachlor	July 2000 triazines	Fall 2000 alachlor	Fall 2000 triazines
SW-1	0.19	0.18	0.14	x	x	x
MW-1	x	x	x	x	x	x
MW-2	0.1	1.4	0.10	0.16	x	x
MW-3	11.0	5.8	12.0	x	11	x
MW-4	15.0	x	27.0	x	34	x
MW-5	0.16	0.18	0.10	2.6	x	x
MW-6	x	x	x	x	0.1	x
MW-7	x	0.23	x	x	x	x
MW-8	0.15	x	0.15	x	x	x
MW-9	0.11	x	0.21	x	0.1	x
MW-10	x	x	0.11	x	x	x
MW-11	0.32	x	0.33	x	0.09	x
MW-12	---	---	0.32	x	x	x
MW-13	---	---	1.4	x	x	x
MW-14	---	---	0.10	x	x	x
MW-15	0.10	x	0.11	x	x	x
TD-1	x	0.84	x	0.45	x	0.3
TD-2	x	0.28	---	---	---	---
TD-3	x	0.21	0.10	0.47	x	0.3
TD-4	0.18	3.9	0.11	2.1	0.1	4.0
TD-5	x	0.57	x	0.26	x	x
TD-6	x	1.0	x	x	x	x
TD-7	x	4.2	---	---	x	0.3
TD-8	x	0.84	x	1.9	x	0.5

Dashes (---) indicate no test conducted; x = below detection limits.

indicate the metolachlor ESA (ethanesulfonic acid) metabolite (Seybold et al., 2001) is likely present since the concentrations are below the LLD for metolachlor. The LLD for metolachlor is 0.6 ppb while the LLD for metolachlor ESA is 0.08 ppb. MW-3 and MW-4 values are obvious exceptions and discussed separately near the end of this section. Metolachlor, if being transported to surface water via tile drainage or present in monitoring wells, is below the detection limit. Detections from the alachlor test were reported for Nottawa Creek surface water June and July 2000 but not September 2000.

There are significantly more detections from the alachlor test in monitoring wells than in tile drains. This is somewhat perplexing and may perhaps be explained as a consequence of the immunoassay testing detection limits. One possible theory is that metolachlor could be present in some tile drains at a concentration less than the LLD of 0.6 ppb. If metolachlor degradation had not yet occurred, metolachlor ESA would not be detected. Upon further vertical transport metolachlor degradation could occur, accounting for metolachlor ESA detection in monitoring wells.

The results for triazines detected in monitoring wells are shown in Figure 46. Nottawa Creek surface water concentrations are also plotted for reference. In this figure, only wells with detections have been plotted. In other words, of the 15 monitoring wells, only 4 had triazines detected. Two possible explanations are degradation of triazines being before reaching the water table or triazines being sorbed to soil particles.

On the other hand, triazines are being transported shortly after application by

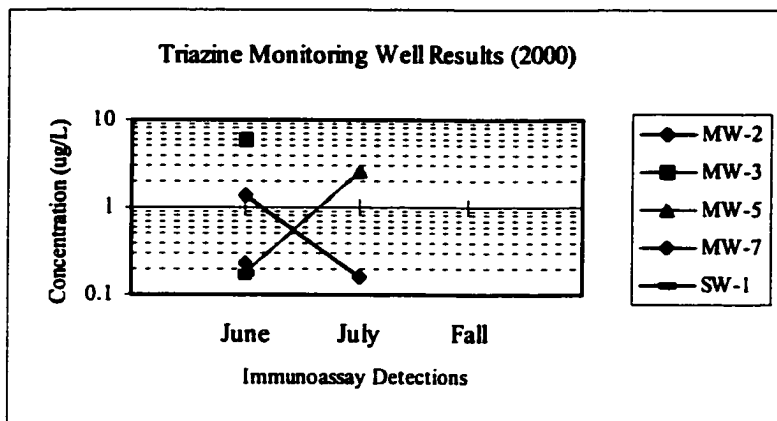


Figure 46. Year 2000 Triazine Monitoring Well Immunoassay Results.

tile drainage as shown in Figure 47. All tile drains showed triazine detections.

Comparatively, atrazine has a lower LLD (0.02 ppb) than metolachlor (LLD 0.6 ppb) which may account for some of the detection discrepancies between the two compounds. Detections from the triazine test were reported for Nottawa Creek surface water June 2000 but not for the July or fall 2000 sampling events.

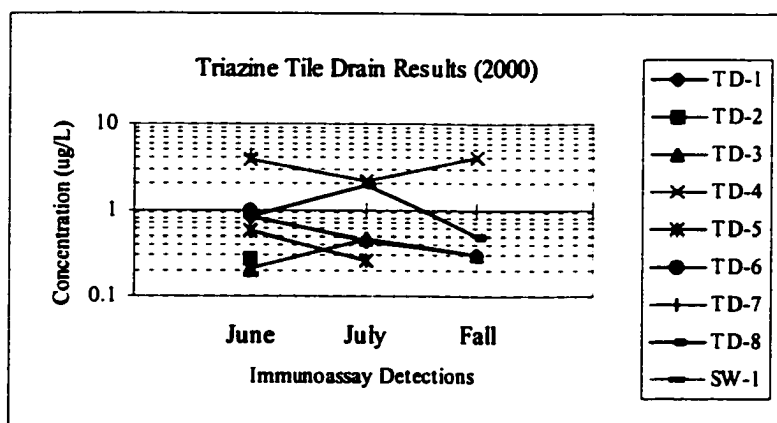


Figure 47. Year 2000 Triazine Tile Drain Immunoassay Results.

The peak concentrations for both alachlor and triazines occur shortly after application as detected by the June and July sampling events. By early fall, there is generally a lack of detections in both monitoring wells and tile drains.

A limited number of samples were collected for GC/MS and LC/MS analysis for 2001. The results for June and July 2001 are shown in Table 20. There were 13

Table 20

June and July 2001 GC/MS Results (Concentrations in μL)

Date	June 2001	June 2001	July 2001
chemical name	atrazine	simazine	atrazine
LLD (μL)	0.1	0.1	0.5
SW-1	0.2	0.9	x
MW-1	---	---	x
MW-2	x	x	x
MW-3	0.1	x	x
MW-5	0.1	x	x
MW-7	0.8	x	x
MW-12	x	x	x
MW-13	x	x	x
TD-1	x	x	x
TD-2	x	x	x
TD-4	0.5	x	x
TD-5	---	---	x
TD-6	x	x	x
TD-7	0.1	x	x
TD-8	0.6	x	0.5

x = below detection limits; --- not tested

samples collected for GC/MS analysis for the June 2001 sampling event. For June, the laboratory's lower limit of detection for atrazine and simazine was 0.1 μL .

Atrazine was detected at 0.2 μL and simazine was detected at 0.9 μL for Nottawa Creek surface water. Simazine was not detected in any monitoring wells or tile drains. Out of 6 monitoring wells tested, atrazine was detected in 3 wells. Out of 6 tile drains tested, atrazine was detected in 3 tile drains. All detected atrazine concentrations were below the drinking water standard MCL of 3 μL .

There were 15 samples collected for analysis of atrazine only by GC/MS for the July 2001 sampling event. The LLD was 0.5 μL . Atrazine was not detected for Nottawa Creek surface water. Atrazine was not detected in any of the 7 monitoring wells tested. Out of 7 tile drains tested, atrazine was detected in 1 tile drain (TD-8) at a concentration 0.5 μL .

Selected samples collected in September 2001 were analyzed by the USGS Organic Geochemistry Research Laboratory (Lawrence, KS) for various corn and soybean herbicides and degradation products (Table 21). The majority of metabolites are ESA (ethane sulfonic acid) and OXA (oxanilic acid) breakdown products. The samples were analyzed by GC/MS and LC/MS methods.

For September 2001, GC/MS results were reported for Nottawa Creek surface water and MW-6, MW-8, MW-9, MW-10, and MW-11. There were no detections above the LLD (lower limit of detection) of 0.05 μL reported for any of these samples analyzed by GC/MS methods. LC/MS results are reported for 6 monitoring wells (Table 22), 4 tile drains, and September 8 and 9 samples (1a and 1b) of Nottawa Creek surface water (Table 23). Concentration values are listed for samples analyzed by LC/MS methods only if concentrations were detected above the LLD of 0.05 μL .

Table 21

**Corn and Soybeans Herbicides Analyzed for by GC/MS Methods (LLD 0.05 μ /L) and
Acetamide Degradation Products Analyzed for by LC/MS Methods (LLD 0.05 μ /L)**

GC/MS	GC/MS	LC/MS
Acetochlor	Metolachlor	Acetochlor ESA
Alachlor	Metribuzin	Acetochlor OXA
Ametryn	Pendimethalin	Alachlor ESA
Atrazine	Prometon	Alachlor OXA
Cyanazine	Prometryn	Dimethenamid ESA
Cyanazine Amide	Propachlor	Dimethenamid OXA
Deethylatrazine	Propazine	Flufenacet ESA
Deisopropylatrazine	Simazine	Flufenacet OXA
Dimethenamid	Terbutryn	Metolachlor ESA
Flufenacet		Metolachlor OXA

Table 22

LC/MS Results for Monitoring Wells (Concentrations in μ /L)

	MW-2	MW-6	MW-8	MW-9	MW-10	MW-11
Alachlor ESA	0.17		0.07	0.16	0.05	1.77
Alachlor OXA						0.15
Metolachlor ESA	9.72		2.36	0.14	1.12	1.41
Metolachlor OXA						0.10

Table 23

LC/MS Results for Nottawa Creek and Tile Drains (Concentrations in μ /L)

	SW-1a	SW-1b	TD-1	TD-4	TD-6	TD-8
Acetochlor ESA				0.07		
Acetochlor OXA				0.09		
Alachlor ESA	0.75	0.73	0.06	0.13		0.08
Alachlor OXA				0.06		
Dimethenamid ESA				3.85		0.85
Dimethenamid OXA				6.53		0.15
Metolachlor ESA	0.55	0.55	2.74	5.64	5.74	2.83
Metolachlor OXA	0.07	0.08	0.35	5.99	0.17	

Triazine detections by immunoassay for 2000 along with GC/MS and LC/MS results from 2001 seem to verify the trend in declining herbicide concentrations and detections with time after application. For September 2001, no triazine parent compounds or breakdown products were detected in 2 Nottawa Creek surface water samples or the 2 streambed well samples analyzed by GC/MS methods (see Table 21). In addition, there were no detections of other parent corn and soybeans herbicides in Nottawa Creek surface water. However, alachlor and metolachlor metabolites were detected in Nottawa Creek surface water and the 2 streambed wells September 2001.

Analysis by LC/MS reported September 2001 Nottawa Creek surface water detections for herbicide degradation products of 0.75 and 0.73 μL for alachlor ESA, 0.55 and 0.55 μL for metolachlor ESA, and 0.07 and 0.08 μL for metolachlor OXA. Analysis by LC/MS reported September 2001 MW-10 (streambed well) detections for herbicide degradation products of 0.05 μL for alachlor ESA and 1.12 μL for metolachlor ESA. September 2001 MW-11 (streambed well) detections were reported for herbicide degradation products of 1.77 μL for alachlor ESA, 0.15 μL for alachlor OXA, 1.41 μL for metolachlor ESA, and 0.10 μL for metolachlor OXA. The results listed above are likely to be representative of the watershed as a whole, because Nottawa Creek may be considered as an agricultural stream.

Metolachlor detections for sites sampled on the farm could be expected to drop below the detection limit because metolachlor was not used on the farm in 2001. While metolachlor was not detected in any September samples, its breakdown

products were reported for monitoring well and tile drain samples (see Tables 22 and 23).

Dimethenamid [2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide] is a relatively new herbicide (Zimmerman et al., 2002) and was first used on the farm in 2001 on corn. Dimethenamid does not have a USEPA MCL. The parent compound, dimethenamid, was not detected for samples analyzed September 2001 but its breakdown products were detected for TD-4 at concentrations of 3.85 μL for dimethenamid ESA and 6.53 μL for dimethenamid OXA, and for TD-8 at concentrations of 0.85 μL for dimethenamid ESA and 0.15 μL for dimethenamid OXA.

It is somewhat surprising breakdown products of both acetochlor and alachlor were detected in water samples from monitoring wells and tile drains September 2001. Acetochlor and alachlor were not used on the farm in at least the past 4 years. The farm is within an area of intensive agricultural activity and one possibility is that the contaminants are transported in flowing groundwater from adjacent areas. Several studies cited by Zimmerman et al. (2002) suggest the ESA degradate of alachlor has substantially less toxicity than the parent compound, which has a USEPA MCL of 2 μL .

To review, the immunoassay results for 2000 were not verified. It must be restated that immunoassay methods are screening tools and should be verified with approved USEPA analytical methods, such as GC/MS and LC/MS. One possible error with immunoassay techniques is cross reactivity between compounds (Elisabeth

Scribner, USGS, personal comm., 2001). Submitted immunoassay samples were also initially frozen and later thawed for analysis. In light of these or other possible errors, the anomalous results for MW-3 and MW-4 will now be discussed.

MW-3 is a shallow well next to the compost pile while MW-4 is a shallow well adjacent to the lagoon. Some confined swine feeding operations occur adjacent to the unlined lagoon and have a waste discharge pipe leading to the lagoon. Animal waste from swine confined feeding operations is composted along with some straw and/or wheat stem bedding materials to provide an additional carbon source.

Barbash and Resek (1996) cite monitoring studies that suggest relations between proximity near feedlots and barnyards and herbicide detections in groundwater. Barbash and Resek (1996) reported the frequency of detection and greatest concentrations of triazine and acetanilide herbicides detected in groundwater were most dramatic within 6 m of the operation but still detectable within sight. This study was established through the Cooperative Private Well Testing Program and based on immunoassay analyses (Barbash and Resek, 1996). Barbash and Resek (1996) suggested that either herbicides may be present in feed or other plant material ingested by livestock or in some cases could be a matter of pesticide mixing areas being in close proximity to confined feeding operations.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

This final chapter comprises an integrated assessment of this research and other information resources in the watershed (Kehew et al., 1999; Dannemiller and Baltusis, 1990) to formulate a general water quality report for the Nottawa Creek Watershed. Conclusions and recommendations are discussed and summarized below.

1. Residents in the thin drift area should have their wells tested annually for nitrate. A mid-June sampling date may be preferred because that was usually when nitrate concentrations were the highest for monitoring wells. In addition, sampling should be done shortly after significant precipitation and recharge events. Nitrate is generally transported through the unsaturated zone to the water table after the soil becomes saturated. It is most desirable to sample when the potential for nitrate concentrations in groundwater are high, because sampling is usually done very infrequently.

Three out of the four private wells sampled for the dissertation study tested above the MCL for nitrate as nitrogen. Unlike public water systems, whose drinking water is regulated by the USEPA, private well operators alone are responsible for having their water tested to ensure it is fit for drinking. It became apparent from a recent Nottawa Creek Watershed tour that some citizens are not aware of this.

Monitoring wells in the dissertation study area showed great variance in nitrate concentrations, even for wells within 150 m of each other. Lithology of glacial deposits can vary laterally and vertically within short distances. In a random study of wells throughout the Nottawa Creek Watershed, three of thirteen drift wells tested for elevated concentrations of nitrate with one testing above the MCL (Kehew et al., 1999a). Chemical data from Dannemiller and Baltusis (1990) of two wells screened in the Marshall Sandstone support the Kehew et al. (1999a) study of twenty-two wells screened in bedrock of reducing conditions in which nitrate would not be stable.

Recommended nitrate sampling events for future studies of the Nottawa Creek Watershed could follow the timing guidelines above to minimize costs. The two real-time weather stations are excellent indicators of precipitation for the watershed because the Athens station is located at the southwestern portion of the watershed whereas the Ceresco station is located in the northeastern section. These suggestions are based on economic considerations. Muldoon and Madison (2000), in their study based on automated sampling, stated periodic sampling events only can miss detection of peak concentrations.

2. Residents in the thin drift area should have their wells tested annually for the triazine herbicides (atrazine and simazine) and the acetamide herbicides (alachlor, acetochlor, metolachlor, and dimethenamid) based on this study. Three out of four monitoring wells sampled, for the dissertation study, had water samples test positive for atrazine June 2001 by USEPA approved GC/MS (gas chromatography/mass spectrometry) laboratory methods. Atrazine is applied to both corn and soybean

fields, although glyphosate is frequently used instead of atrazine for soybeans.

Simazine was not used on the farm but was detected in Nottawa Creek surface water June 2001 by GC/MS analysis. Degradation products of the herbicides alachlor, acetochlor, metolachlor, and dimethenamid were detected by LC/MS (liquid chromatography/mass spectrometry) methods in Nottawa Creek surface water, monitoring wells, and/or tile drain samples September 2001. Some people feel the standards and guidelines established by the USEPA for pesticides in drinking water provide an adequate margin of safety for human health (USGS, 1999). Other people feel the presence of any pesticides in drinking water is unacceptable (USGS, 1999). Immunoassay test kits provide an economical means of screening for triazine and acetamide herbicides (approximately \$15/sample) and are widely available. If a sample tests positive, or above a certain limit, it should be verified by GC/MS or LC/MS analysis. Sampling recommendations for triazine and acetamide herbicides are generally the same as for nitrate.

3. Immunoassay testing implies that a seasonal herbicide detection peak occurs in June-July and tapers off dramatically in early fall. This was substantiated by GC/MS and LC/MS methods in which only metolachlor and alachlor metabolites were detected in streambed wells and Nottawa Creek surface water for September 2001. Atrazine and other triazine herbicides were not detected in streambed wells and Nottawa Creek surface water for September 2001 for the LLD of 0.05 μ /L.

A recommendation for future study is automated sampling of Nottawa Creek surface water utilizing composited samples collected for herbicide analysis. This

could help define peak concentrations due to agricultural practices and seasonality. These patterns tend to repeat each year (USGS, 1999). The recommended sampling interval could range from May to August. This pattern for peak concentrations has been observed in many agricultural streams and is known as the spring flush (Zimmerman et al., 2002).

As an alternative to automated sampling, it is suggested Nottawa Creek be sampled for herbicides in late May or June. This time period coincides with herbicide applications. Precipitation amounts reported by the remote weather stations could indicate which portions of Nottawa Creek to sample because maximum herbicide concentrations are associated with runoff following application. One of the main limitations of the dissertation study was the requirement the laboratory be notified one week in advance. Consequently, it was not possible to select the most appropriate time to sample for detection of peak concentrations.

One BMP suggestion to help remove or filter pesticides, as well as nutrients, is to improve or increase the size of the riparian buffer strip along Nottawa Creek. Sorption onto organic particles can help prevent pesticides from entering Nottawa Creek. Another BMP suggestion is to apply less pesticides to highly sloped areas and areas near waterways, such as drainage ditches. Runoff from highly sloped areas can also lead to greater accumulations of pesticides in flatter areas, with possible infiltration of pesticides to groundwater. A last BMP suggestion is to rotate crops frequently. This could lessen the buildup of a particular herbicide and allow more time for eventual degradation to carbon dioxide and water.

4. Immunoassay and GC/MS analysis suggests triazines are likely leached vertically via preferential flow and transported to surface water by tile drains. For June of 2000, all 8 tile drains showed triazine detections by immunoassay. For the June 2001 sampling event, out of 6 tile drains tested, atrazine was detected in 3 tile drains by GC/MS analysis. Atrazine was detected at 0.2 μL and simazine was detected at 0.9 μL for Nottawa Creek surface water by GC/MS analysis June of 2001. Simazine was not detected in any tile drains from the farm.

5. Low or non-detect triazine concentrations by immunoassay and GC/MS analysis in monitoring wells suggest significant degradation or retardation compared to tile drains. Out of 12 monitoring wells tested by immunoassay June of 2000, 4 tested positive for triazines. For the June 2001 sampling event, out of 6 monitoring wells tested by GC/MS analysis, atrazine was detected in 3 wells. Out of 15 monitoring wells tested by immunoassay July of 2000, 2 tested positive for triazines. For the July 2001 sampling event, out of 7 monitoring wells tested, atrazine was not detected in any wells by GC/MS analysis.

6. Analysis for atrazine by GC/MS suggests triazine detections by immunoassay may be mostly atrazine degradation products and not atrazine itself. For June of 2000, all 8 tile drains showed triazine detections by immunoassay. Comparatively, for the June 2001 sampling event, out of 6 tile drains tested, atrazine was detected in 3 tile drains by GC/MS analysis. For July of 2000, 5 out of 6 tile drains sampled showed triazine detections by immunoassay. Comparatively, for the July 2001 sampling event, out of 7 tile drains tested, atrazine was detected in only 1

tile drain by GC/MS analysis.

7. Immunoassay chloroacetanilide (acetamide) results indicated a much greater detection in wells compared to triazines but were largely undetected or at low concentrations in tile drains. This may perhaps be explained as a consequence of the immunoassay testing detection limits. One possible theory is that metolachlor could be present in some tile drains at a concentration less than the method reporting limit of 0.6 ppb. If metolachlor degradation had not yet occurred, metolachlor ESA would not be detected. Upon further vertical transport metolachlor degradation could occur, accounting for metolachlor ESA detection in monitoring wells. The immunoassay method reporting limit for metolachlor ESA is 0.08 μL .

8. Analysis by immunoassay implied the metolachlor ESA metabolite was likely detected in most observation wells, tile drains, and surface water, rather than metolachlor, the parent compound. Out of 31 acetamide immunoassay detections for the year 2000, 24 were below the method detection limit for metolachlor (0.6 μL) whereas 7 were above. Again, the immunoassay method reporting limit for metolachlor ESA is 0.08 μL .

9. Analysis of herbicides by GC/MS and LC/MS for September 2001 support the immunoassay results for September-October 2000 in that herbicide detections taper off dramatically in late summer-early fall. Only degradation products were reported for selected samples analyzed for September 2001.

For September 2001, GC/MS results were reported for Nottawa Creek surface water and MW-6, MW-8, MW-9, MW-10, and MW-11. There were no triazine

detections above the method reporting limit of 0.05 μL for any of these samples.

LC/MS results are reported here for September 8 and 9 samples of Nottawa Creek surface water, the two streambed wells, and one tile drain. Results for 3 other monitoring wells and 3 tile drains are listed in the text (see Tables 22 and 23). The results for the streambed wells and Nottawa Creek surface water are likely to be representative of the watershed as a whole, because Nottawa Creek may be considered as an agricultural stream.

Analysis by LC/MS reported September 2001 Nottawa Creek surface water detections for herbicide degradation products of 0.75 μL for alachlor ESA, 0.5 μL for metolachlor ESA, and 0.07 μL for metolachlor OXA. No triazines were detected for the method detection limit of 0.05 μL .

Analysis by LC/MS reported September 2001 MW-10 (streambed well) detections for herbicide degradation products of 0.05 μL for alachlor ESA and 1.12 μL for metolachlor ESA. No triazines were detected for the method detection limit of 0.05 μL .

Analysis by LC/MS reported September 2001 MW-11 (streambed well) detections for herbicide degradation products of 1.77 μL for alachlor ESA, 0.15 μL for alachlor OXA, 1.41 μL for metolachlor ESA, and 0.10 μL for metolachlor OXA. No triazines were detected for the LLD of 0.05 μL .

Analysis by LC/MS reported September 2001 TD-4 detections for herbicide degradation products of 0.07 μL for acetochlor ESA, 0.09 μL for acetochlor OXA,

0.13 μL for alachlor ESA, 0.06 μL for alachlor OXA, 3.85 μL for dimethenamid ESA, 6.53 μL for dimethenamid OXA, 5.64 μL for metolachlor ESA, and 5.99 μL for metolachlor OXA. No triazines were detected for the method detection limit of 0.05 μL .

10. Tile drains were a major contributor of nitrate to Nottawa Creek, yet Nottawa Creek nitrate concentrations were consistently low, probably due to dilution. Tile drains were a major contributor of phosphorus to Nottawa Creek only during spring thaw and heavy runoff episodes after fertilizer application. Despite this, Nottawa Creek phosphorus concentrations were also consistently low. This could be due to timing of sampling events. The lab had to be notified one week in advance.

BMPs suggested here include planting of cover crops and soil testing for nitrogen and phosphorus. A cover crop of oats planted after the fall corn harvest appeared to help hold nutrients. Lowest nutrient concentrations were observed for this field for the December 1999 sampling event. This was also partially due to the unseasonably dry fall.

11. Groundwater is likely denitrified before discharging into Nottawa Creek. Tritium results from the two streambed wells, which were uncontaminated with nitrate, indicate groundwater discharging into Nottawa Creek is post-bomb water. The low redox potential of the streambed wells indicate nitrate is probably being reduced before discharging into the dissertation study area of the stream.

12. Precipitation records compared with well water levels indicate significant amounts of shallow groundwater recharge can occur in summer. This has important

implications for residents within the thin drift area. Recharge events occurring during June coincide with fertilizer applications. It is generally assumed most recharge occurs during fall and spring due to evapotranspiration. GLEAMS modeling substantiated the notion of summer recharge with utilization of actual daily temperature and precipitation values, along with other physical and climatic input parameters.

13. δD and $\delta^{18}O$ data suggest tile drains and most monitoring wells respond very quickly to recharge events. $\delta^{18}O$ data from Kehew et al. (1999) and Dannemiller and Baltusis (1990) of bedrock wells suggest -10‰ or less may represent a mixing of fully evolved groundwater whereas greater than -10‰ may have more of a direct recharge path and hence greater vulnerability to surface contamination. Below a depth of 100 ft the aquifers are well mixed (Kehew et al., 1999; Dannemiller and Baltusis, 1990). $\delta^{13}C_{DIC}$ data indicate carbonate dissolution does not follow the usual open or closed pathway. Regarding aquifer vulnerability, infiltrating water may reach tiles quickly after leaving the soil zone. A recommendation for future study of O, H, and C stable isotopes would be to sample monthly for a year. This could lead to a better understanding of recharge and carbon cycling.

14. The triangular finite element groundwater flow model supported the conceptual model in that shallow groundwater is likely intercepted and discharged to surface drains. The model was limited by lack of detailed analysis for hydraulic conductivity and transmissivity outside of the water quality study area.

15. Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ from nitrate from most wells and tile drains suggest that field-applied synthetic fertilizer, composted manure, and liquid manure is transformed or not present. In other words, nitrate was not detected in water samples with the same isotopic signature as applied fertilizer.

Appendix A
Logs of Test Holes

Description of soils and bedrock from wells drilled by Western Michigan University

Notes: (1) Water level measurements are from low flow conditions of December 12, 1999. (2) All color descriptions were determined by comparing color of fresh well cuttings to Munsell soil color charts (1994 revised edition). (3) The agricultural fields where test holes were drilled contain discontinuous surficial deposits of gravel and boulders. (4) All samples contained some gravel of pebble size. (5) The vast majority of grains may be described as sub-angular to sub-rounded. (6) Grain size descriptions are based on sieving and hydrometer analysis. (7) Soil organic matter (OM) is from a 1997 soil analysis report (Midwest Laboratories, Inc., Omaha, NE).

Well number	Lithology	Depth feet
MW-1		
(Static water elevation: 889.8 feet)		
(Cased to 9.8 feet)		
(Depth to water 6.5 feet)		
	Glacial deposits:	
	Silty sand, dark yellowish brown, very poorly sorted, 1.7% OM, 0.7% clay	0-2
	Coarse sand, dark yellowish brown, moderately sorted, 0.1% clay	2-6
	Silty coarse to medium sand, dark gray, moderately sorted, 2.0% clay	6-9
	Coldwater Shale Formation:	
	Silt, gray, moderately sorted, 6.2% clay (split spoon sample)	9-10

Well number	Lithology	Depth feet
MW-2 (Static water elevation: 906.0 feet) (Cased to 17.4 feet) (Depth to water 10.3 feet)		
	Glacial deposits:	
	Medium sand, light olive brown, very poorly sorted, 1.7% OM, 2.4% clay	0-2.5
	Silty medium to fine sand, light olive brown, very poorly sorted, 3.0% clay	2.5-7
	Silty medium to fine sand, olive brown, very poorly sorted, 2.6% clay	7-11.5
	Silty fine to medium sand, light olive brown, poorly sorted, 3.5% clay	11.5-14
	Silty medium to fine sand, gray, poorly sorted, 3.8% clay	14-16
	Silty medium to fine sand, gray, poorly sorted, 4.4% clay (split spoon sample):	16-17.4

Well number	Lithology	Depth feet
MW-3		
(Static water elevation: 907.3 feet)		
(Cased to 15.8 feet)		
(Depth to water 9.0 feet)		
Glacial deposits:		
	Medium sand, brown, poorly sorted, 1.7% OM, 0.1% clay	0-2.5
	Medium sand, dark yellowish brown, poorly sorted, 1.1% clay	2.5-5
	Silty coarse to medium sand, yellowish brown, poorly sorted, 1.8% clay	5-10
	Silty medium to fine sand, light yellowish brown, poorly sorted, 4.2% clay	10-11.5
	Silty medium to fine sand, pale brown, poorly sorted, 5.4% clay	11.5-15.8

Well number	Lithology	Depth feet
MW-4		
(Static water elevation: 901.3 feet)		
(Cased to 15 feet)		
(Depth to water 6.9 feet)		
Glacial deposits:		
	Silty medium to fine sand, light yellowish brown, poorly sorted, 2.5% OM, 2.0% clay	1-3
	Medium to fine sand, brown, poorly sorted, 0.6% clay	3-7
	Medium to coarse sand, light olive brown, poorly sorted, 0.8% clay	9-10
	Silty medium to fine sand, light olive brown, poorly sorted, 4.2% clay	10-14
	Silty fine to very fine sand, light olive brown, poorly sorted, 3.7% clay	14-15

Well number	Lithology	Depth feet
MW-5		
(Static water elevation: 910.5 feet)		
(Cased to 24.0 feet)		
(Depth to water 10.0 feet)		
Glacial deposits:		
	Medium sand, yellowish brown, moderately sorted, 1.9% OM, 0.7% clay	0-4
	Silty medium sand, light olive brown, poorly sorted, 4.1% clay	4-9
	Silty coarse to medium sand, light olive brown, poorly sorted, 1.8% clay	9-16
	Silty medium to fine sand, gray, poorly sorted, 5.7% clay	16-19
	Silty medium to fine sand, gray, poorly sorted, 6.0% clay	19-24

Well number	Lithology	Depth feet
MW-6 (Static water elevation: 905.3 feet) (Cased to 23.1 feet) (Depth to water 9.9 feet)		
	Glacial deposits:	
	Medium to fine sand, light yellowish brown, poorly sorted, 1.8% OM, 0.3% clay	0-3
	Silty medium to fine sand, light olive brown, poorly sorted, 1.5% clay	3-7
	Silty medium to fine sand, light olive brown, poorly sorted, 3.0% clay	7-12
	Silty fine sand, light olive brown, poorly sorted, 1.4% clay	12-23

Well number	Lithology	Depth feet
MW-7 (Static water elevation: 903.8 feet) (Cased to 23.2 feet) (Depth to water 5.8 feet)		
	Glacial deposits:	
	Silty fine to medium sand, light olive brown, poorly sorted, 1.8% OM, 0.5% clay	0-5
	Silty medium to fine sand, light brownish gray, poorly sorted, 3.2% clay	5-12
	Silty medium to fine sand, gray, very poorly sorted, 1.3% clay	12-23

Well number	Lithology	Depth feet
MW-8 (Static water elevation: 892.5 feet) (Cased to 18.6 feet) (Depth to water 10.8 feet)		
	Glacial deposits:	
	Medium to coarse sand, brown, poorly sorted, 1.8% OM, 0.3% clay	0-5
	Sandy gravel, brown, moderately sorted, 0.5% clay	5-9
	Silty medium to coarse sand, yellowish brown, moderately sorted, 0.8% clay	9-14
	Silty coarse to medium sand, yellowish brown, moderately sorted, 0.8% clay	14-19

Well number	Lithology	Depth feet
MW-9 (Static water elevation: 892.6 feet) (Cased to 18.8 feet) (Depth to water 8.1 feet)		
	Glacial deposits:	
	Coarse sand, brown, well sorted, 1.5% OM, 0.1% clay	0-5
	Coarse sand, brown, moderately well sorted, 0.2% clay	5-9
	Silty coarse to medium sand, yellowish brown, poorly sorted, 1.3% clay	9-14
	Sandy gravel, yellowish brown, moderately sorted, 0.9% clay	14-19

Appendix B
Chemical Parameter Values

Chemical Composition Data of the Study Area, December 12, 1999

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	SW-1
pH units	7.40	7.35	7.59	7.29	7.86	7.58	7.54	7.43	6.92	7.98
T (°C)	6.6	9.4	6.0	5.7	6.4	9.0	6.8	10.4	10.4	4.2
C (µS/cm)	590	600	580	2460	560	610	540	610	740	610
DO	---	---	---	---	---	---	---	---	---	---
TDS	---	---	---	1600	280	320	300	350	400	400
HCO ₃	---	---	289	878	153	179	257	269	348	291
Ca	---	---	66.8	165	43.7	61.2	114	81.6	92.3	81.5
SO ₄	---	---	18	130	74	31	38	26	19	45
Cl	---	---	9	139	8	6	3	15	19	16
Mg	---	---	23.4	74	29.2	10.4	34.2	17.1	19	22.3
Na	---	---	6.2	59.6	5.9	3.3	4.9	3.8	4.6	6.5
NO ₃ -N	3.0	0.05	3	50	0.01	---	0.02	7.6	0.01	0.76
TOC	1.5	8	1.9	23	3.2	---	1.7	1.1	4.3	4.6
Fe	---	---	0.57	0.027	0.65	0.05	0.104	0.03	2.33	0.04
K	---	---	1.5	324	1.4	1.1	1.3	0.8	1.7	1.4
Total P	0.03	0.02	0.15	0.04	0.23	---	0.04	0.08	0.31	0.01
NH ₃ -N	x	0.1	x	6.6	x	---	0.02	x	0.1	0.05

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, March 12, 2000

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	SW-1
pH units	7.13	7.07	7.35	6.93	8.89	7.18	7.61	7.16	7.36	8.01
T (°C)	---	6.6	7.3	4.8	8.7	9.2	9.8	10.6	9.3	8.5
C (μS/cm)	---	880	560	4110	300	540	500	610	590	590
DO	---	---	---	---	---	---	---	---	---	---
TDS	490	970	610	4700	310	550	480	800	660	570
HCO ₃	161	366	290	1016	89	169	261	348	350	280
Ca	55.3	112	70.4	250	38.1	64.1	61.3	95.7	90.5	80.9
SO ₄	39	98	21	121	50	35	39	39	18	52
Cl	6	16	8	291	6	5	3	16	18	16
Mg	16.8	35.7	26.1	132	21.6	22.5	22.3	21.7	19.5	22.4
Na	18.8	6.8	5.4	120	7.5	3.7	5.2	4.6	4.4	6.2
NO ₃ -N	9.9	0.06	5.8	150	0.02	18	0.02	2.3	0.07	1.09
TOC	1.4	1.6	1	34	2.9	0.9	1	2.1	5.3	5.7
Fe	0.58	x	0.89	0.01	1.8	1.6	0.2	0.01	1.75	0.01
K	4	1.4	1.4	433	1.4	1	1.1	0.8	1.5	1.2
Total P	0.087	0.32	0.052	0.06	0.189	0.077	0.145	0.006	0.029	0.015
NH ₃ -N	x	0.04	x	31	0.03	x	0.02	x	0.07	0.06

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, March 19, 2000

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8
pH units	7.54	---	7.68	7.12	7.05	7.27	7.35	7.33
T (°C)	6.1	---	6.6	6.7	7.2	6.6	6.8	6.5
C (μS/cm)	540	---	530	610	580	460	540	1150
TDS	400	---	370	420	360	340	390	890
HCO ₃	169	---	239	242	181	203	246	292
Ca	73.9	---	76.8	83.2	---	65.5	76.3	160
SO ₄	33	---	40	39	36	43	43	10
Cl	9	---	11	28	8	8	13	197
Mg	21.5	---	21.3	23.4	---	20.6	22.2	35.4
Na	4.6	---	3.7	8.5	---	7.4	3.7	20.2
NO ₃ -N	25	---	10	16	20	11	7.4	7.9
TOC	1.0	---	2.2	8.0	1.9	2.7	1.6	2.2
Fe	x	---	x	0.12	---	x	x	x
K	0.8	---	0.08	5	---	0.6	0.6	1.4
ortho-P	x		x	0.23	0.01	0.02	x	0.01
Total P	0.02	---	x	0.39	0.01	0.03	x	0.01
NH ₃ -N	x	---	x	0.8	x	0.1	x	x

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, May 13-14, 2000

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	SW-1
pH units	7.22	7.10	7.29	6.76	7.82	7.11	7.18	7.06	6.95	7.37
T (°C)	9.6	10.9	10.4	10.1	10.3	10.5	10.0	9.8	9.5	13.0
C (μS/cm)	490	820	510	3530	330	430	390	570	540	470
DO	3.23	1.13	2.98	0.19	0.95	3.46	2.01	0.20	0.17	8.53
NH₃-N	0.03	0.06	x	23	0.01	x	x	x	0.09	0.05
NO₃-N	0.47	0.29	7.9	170	x	21	0.17	2.8	0.62	1.17
Total P	0.74	0.12	0.02	0.05	0.03	0.04	0.02	0.02	0.06	0.04
TOC	4.8	2.4	1.8	33	2.4	0.9	1.2	4.7	4.7	12

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13
pH units	6.82	7.10	7.07	6.91	7.05	7.01	7.16	7.05	---	---
T (°C)	13.1	13.4	14.3	13.7	13.6	13.2	13.1	13.1	---	---
C (μS/cm)	590	430	420	490	540	430	470	840	---	---
NH₃-N	x	x	x	0.2	x	x	x	x	x	1.5
NO₃-N	41	20	12	27	25	10	11	14	23	8.0
Total P	0.02	0.01	0.11	0.15	0.02	0.05	0.01	0.02	0.02	x
TOC	1.7	1.7	5.8	3.0	2.0	2.7	2.1	2.4	3.1	3.7

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, June 11-18, 2000

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.53	7.54	7.57	7.22	8.47	7.91	7.55	7.72	7.39	7.51	7.69	7.89
T (°C)	10.8	11.5	11.6	11.2	11.5	11.6	11.7	10.8	11.4	16.0	11.8	19.7
C (μS/cm)	470	770	510	3320	380	470	460	520	450	590	550	480
DO	1.67	0.40	1.51	0.10	0.21	5.49	0.85	0.65	0.18	0.16	0.12	7.01
TDS	400	610	420	3100	300	380	370	440	420	460	520	440
HCO ₃	169	364	289	827	157	167	262	324	334	315	341	274
Ca	74.7	98	74.5	235	35.4	65.2	65.9	103	50.6	96.4	107	87.3
SO ₄	36	97	21	99	65	35	43	35	18	36	46	44
Cl	6	14	10	249	10	5	2	13	19	24	26	14
Mg	15.8	38.6	28.7	125	23.6	22.2	22.3	20.0	6.9	23.5	23.2	22.1
Na	10.3	5.7	4.1	96.7	5.5	2.3	4.5	3.8	2.9	9.6	10.6	5.6
NO ₃ -N	21	0.11	9.3	170	x	18	0.12	3.3	0.57	2.3	x	0.89
TOC	2.2	5.6	5.7	39	4.2	0.6	1.1	6.6	9.0	5.1	6.8	9.2
Fe	x	x	x	x	x	x	0.02	x	3.2	0.19	3.74	0.04
K	3.19	1.74	1.69	326	1.19	0.76	1.16	0.88	0.42	1.34	1.66	1.24
Total P	0.20	0.33	0.18	0.12	0.18	0.06	0.06	0.04	0.07	0.08	0.09	0.03
NH ₃ -N	x	0.05	0.1	18	0.02	x	0.02	x	0.10	x	0.12	0.04

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, June 18, 2000

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-15	SW-1	SW-2
pH units	7.46	7.29	7.23	6.98	6.69	7.27	7.17	7.38	---	8.00	---	7.86
T (°C)	16.9	16.9	16.2	16.1	16.4	15.5	16.9	16.8	---	12.3	---	24.1
C (μS/cm)	440	410	510	650	610	420	530	810	---	550	---	8390
DO	---	---	---	---	---	---	---	---	---	---	---	0.12
TDS	530	400	440	500	500	350	450	720	---	500	---	3700
HCO ₃	92	178	224	195	173	184	234	289	---	238	---	4062
Ca	75.1	73.7	79.4	---	---	58.8	62.6	116	---	89.5	---	---
SO ₄	24	26	40	36	33	36	38	19	---	29	---	54
Cl	10	8	11	28	10	7	9	102	---	14	---	514
Mg	18.6	20.7	20.8	---	---	18.4	22.5	27.4	---	19.2	---	---
Na	3.2	2.8	2.5	---	---	3.3	1.9	11.1	---	7.4	---	---
NO ₃ -N	44	22	14	21	29	12	16	16	---	13	0.98	x
TOC	1.7	1.6	1.8	2.4	1.8	2.2	2.6	3.2	---	2.0	8.8	480
Fe	x	x	x	---	---	x	x	x	---	x	---	---
K	2.14	0.61	1.00	---	---	1.02	0.82	1.99	---	3.32	---	---
Total P	0.02	x	0.02	0.05	0.02	0.04	0.01	0.02	---	x	0.04	120
NH ₃ -N	x	x	x	x	x	0.2	x	x	---	x	0.05	770

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted; SW-1 = stream; SW-2 = lagoon

Chemical Composition Data of the Study Area, July 15-16, 2000

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.88	8.15	7.31	7.41	9.28	7.74	7.86	7.91	7.84	7.80	7.92	7.83
T (°C)	16.3	14.1	14.7	13.3	14.0	16.4	14.0	11.7	13.1	16.2	12.4	19.2
C (μS/cm)	500	710	580	3230	250	490	460	410	480	640	600	540
DO	1.51	0.91	1.14	0.15	0.19	6.95	0.72	2.79	0.13	0.15	0.17	7.56
NO ₃ -N	23	0.23	10	140	0.05	19	0.04	9.7	0.98	1.36	x	0.90
TOC	2.0	1.4	1.3	39	3.8	0.07	0.07	1.4	5.6	3.2	2.8	7.1
Total P	1.9	0.22	0.02	0.13	0.02	0.03	0.08	0.02	0.04	0.07	0.04	0.03
NH ₃ -N	x	0.04	0.1	22	x	x	0.03	x	0.12	0.07	0.12	0.04

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15
pH units	7.55	---	7.03	7.05	7.49	7.25	---	7.89	7.63	7.58	8.37	8.13
T (°C)	20.6	---	17.8	18.3	18.5	18.1	---	18.3	15.0	12.7	11.5	14.3
C (μS/cm)	370	---	490	590	560	470	---	880	1150	850	410	430
DO	---	---	---	---	---	---	---	---	---	---	---	---
NO ₃ -N	43	---	12	17	27	13	---	11	27	11	1.72	12
TOC	1.6	---	2.8	2.5	1.7	2.1	---	3.2	3.7	5.0	2.3	2.2
Total P	0.02	---	0.02	0.03	0.02	0.03	---	0.03	0.01	x	x	x
NH ₃ -N	x	---	x	x	x	x	---	x	0.2	1.7	x	x

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, September 24, 2000

	TD-1	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15	SW-1
pH units	7.26	6.97	6.98	6.94	7.63	7.34	7.10	7.72	7.43	7.31	7.18	7.24
T (°C)	16.4	15.8	16.6	15.9	16.5	16.3	16.1	16.3	14.3	11.6	13.6	14.7
C (μS/cm)	540	590	710	600	340	330	960	1190	820	480	620	560
DO	---	---	---	---	---	---	---	---	---	---	---	---
TDS	370	350	400	360	330	350	730	880	680	320	410	390
HCO₃	143	251	244	200	208	296	494	494	497	333	261	283
Ca	---	79.4	79.4	---	62.9	86.3	137	---	120	68.9	94.4	75.8
SO₄	28	40	37	32	40	46	18	82	73	13	25	43
Cl	7	11	40	8	6	5	124	102	36	2	11	15
Mg	---	22.8	24.0	---	19.5	24.4	30.8	---	39.8	22.4	19.8	21.8
Na	---	3.2	8.3	---	4.1	2.8	12.5	---	19.5	x	5.9	5.4
NO₃-N	26	8.9	12	17	8.7	4.6	6.2	26	9.2	0.56	18	0.71
TOC	1.3	2.1	2.8	2.0	1.9	2.9	2.9	3.1	3.8	1.4	1.6	7.3
Fe	---	0.020	0.027	---	x	x	x	---	x	x	x	0.097
K	---	0.97	3.01	---	0.89	0.91	1.86	---	23	1.62	3.06	1.49
Total P	0.02	0.02	0.06	0.02	0.03	0.02	0.03	0.02	x	x	x	0.02
o-Phos	0.01	0.01	0.04	0.01	0.02	x	0.02	0.01	x	x	x	x
NH₃-N	x	x	x	x	x	x	x	0.02	2.0	x	x	0.03

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, October 1, 2000

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	8.02	7.85	7.97	7.31	8.68	8.37	8.32	8.23	7.73	8.01	8.04	8.22
T (°C)	15.8	14.7	15.2	15.9	15.4	15.5	14.4	14.1	15.0	14.2	12.8	14.9
C (μS/cm)	500	750	600	3170	420	480	480	450	540	620	630	550
DO	0.32	1.02	0.64	0.14	0.15	6.78	0.66	6.32	0.14	0.15	0.13	8.26
TDS	320	510	370	2300	280	310	320	330	410	390	410	400
HCO ₃	192	387	311	911	181	168	272	213	352	328	358	295
Ca	66.7	108	78.7	191	46.1	65.6	69.5	75.7	90.9	86.7	99.7	84.3
SO ₄	36	100	20	115	73	33	40	17	16	39	51	43
Cl	6	15	12	210	11	6	2	6	17	23	27	17
Mg	13.8	39.6	33.8	99.0	37.1	21.2	23.7	15.8	20.2	24.9	23.8	24.8
Na	11.7	5.8	4.4	91.1	4.0	3.0	3.9	2.4	3.7	12.5	10.2	5.0
NO ₃ -N	10	0.07	9.5	120	x	18	0.02	15	0.66	0.38	x	0.79
TOC	2.6	2.8	2.0	35	2.2	0.8	0.9	1.4	5.2	3.0	3.2	5.2
Fe	0.034	0.043	x	x	x	x	x	x	2.60	1.20	3.36	0.038
K	3.95	1.52	1.86	405	1.09	0.67	1.27	0.89	1.76	1.37	2.00	1.57
Total P	0.41	0.30	0.05	0.03	0.18	0.03	0.30	0.04	0.13	0.17	0.04	0.02
o-Phos	0.02	x	x	0.01	x	x	x	x	x	x	x	x
NH ₃ -N	x	0.05	x	17	0.03	x	0.06	x	0.14	0.11	0.14	0.02

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, December 26, 2000

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	SW-1
pH units	7.23	---	6.83	7.11	---	6.34	7.03	7.48	---	---	---	7.54
T (°C)	6.5	---	7.9	8.1	---	6.0	4.5	5.9	---	---	---	0.3
C (μS/cm)	350	---	410	480	---	260	430	650	---	---	---	370
DO	---	---	---	---	---	---	---	---	---	---	---	11.96
TDS	310	---	350	390	---	290	340	580	---	---	---	370
HCO ₃	142	---	257	224	---	208	252	319	---	---	---	295
Ca	---	---	---	84.6	---	---	---	---	---	---	---	89.4
SO ₄	23	---	33	29	---	31	20	12	---	---	---	39
Cl	7	---	10	32	---	6	11	110	---	---	---	15
Mg	---	---	---	22.5	---	---	---	---	---	---	---	22.0
Na	---	---	---	6.7	---	---	---	---	---	---	---	5.8
NO ₃ -N	26	---	8.0	15	---	8.7	11	7.2	---	---	---	0.97
TOC	0.9	---	1.8	1.6	---	1.2	1.6	1.4	---	---	---	6.2
Fe	---	---	---	0.03	---	---	---	---	---	---	---	0.06
K	---	---	---	1.8	---	---	---	---	---	---	---	1.2
Total P	0.014	---	0.014	0.044	---	0.053	0.011	0.017	---	---	---	0.022
o-Phos	x	---	x	0.03	---	0.04	x	0.01	---	---	---	x
NH ₃ -N	x	---	x	x	---	0.03	x	x	---	---	---	0.10

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, December 10, 2000

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	---	---	---	---	---	---	---	---	---	---	---	---
T (°C)	9.7	10.2	9.2	12.2	9.1	7.77	10.7	11.4	10.6	5.7	9.0	3.2
C (μS/cm)	580	740	720	2960	500	610	530	590	670	670	760	540
DO	2.01	2.50	3.71	0.41	1.59	10.8	2.29	5.20	0.79	0.42	0.50	11.89
TDS	340	520	390	2100	310	340	310	340	400	410	470	390
HCO ₃	246	395	329	794	185	169	274	214	359	329	363	305
Ca	64.5	109	85.4	199	41.6	65.1	67.5	77.8	96.6	88.8	107	89.4
SO ₄	36	83	8	62	66	25	35	13	8	35	39	37
Cl	4	14	15	162	10	6	2	10	16	20	28	16
Mg	13.1	38.5	30.4	88	34.4	20.9	23.3	16.7	19.9	24.6	23.0	23.2
Na	24.6	6.8	5.6	70.5	5.5	3.7	5.9	3.4	4.6	10.8	11.5	6.1
NO ₃ -N	8.9	0.39	10	140	x	18	0.04	15	0.98	0.96	x	0.96
TOC	1.8	1.7	1.8	32	3.5	0.6	0.8	1.0	4.7	2.6	2.6	5.6
Fe	x	x	x	x	x	x	x	x	2.46	1.2	3.64	0.036
K	3.5	1.2	1.6	343	1.1	0.6	1.2	0.8	1.6	1.0	1.8	1.3
Total P	0.05	0.28	0.34	0.04	0.26	0.06	0.40	0.05	0.07	0.05	0.02	0.01
o-Phos	0.02	x	x	0.02	x	x	x	x	0.01	x	x	x
NH ₃ -N	x	0.04	x	8.8	0.02	x	0.03	x	0.14	0.07	0.14	0.09

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, March 11, 2001

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.39	7.66	7.64	6.89	7.94	8.00	7.78	6.91	7.02	7.15	7.27	7.57
T (°C)	5.7	7.5	7.7	8.3	6.2	6.5	7.3	8.8	7.4	6.2	7.4	5.1
C (μS/cm)	280	460	420	1590	280	350	380	230	340	440	270	310
DO	1.52	2.58	3.69	0.62	0.71	7.87	1.76	4.79	0.67	0.52	0.62	10.51
TDS	340	460	400	2000	340	300	320	340	390	400	470	350
HCO ₃	209	324	313	628	231	164	269	203	345	302	348	245
Ca	62.5	92.9	83.6	197	57.0	62.8	67.1	78.5	92.8	85.8	101	77.2
SO ₄	41	70	16	104	68	28	38	14	15	36	44	38
Cl	5	10	17	131	9	6	2	9	18	19	29	14
Mg	17.3	32.6	30.3	88	33.5	20.2	22.6	17.0	19.6	23.2	22.4	18.9
Na	8.9	5.5	4.7	58.6	4.6	3.8	4.4	3.3	4.8	13.4	11.4	5.1
NO ₃ -N	1.80	4.4	11	140	0.04	18	0.10	19	0.43	3.5	0.02	1.29
TOC	0.81	2.7	1.9	28	2.7	0.72	0.78	1.1	4.9	2.0	3.1	8.0
Fe	x	x	x	x	0.110	x	x	x	2.3	0.3	3.5	0.14
K	1.9	1.0	1.3	294	0.9	0.4	1.0	0.7	1.5	1.0	1.7	1.2
Total P	0.13	0.45	0.04	0.09	0.08	0.05	0.31	0.02	0.05	0.03	0.02	0.02
o-Phos	0.01	x	x	x	x	x	x	x	x	x	x	x
NH ₃ -N	0.06	0.01	x	5	0.01	x	0.03	x	0.12	0.04	0.16	0.05

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, March 18, 2001

	TD-1	TD-2	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15	SW-1
pH units	6.94	6.80	7.17	---	7.13	7.33	7.41	6.84	7.09	7.38	7.25	7.68
T (°C)	5.7	7.4	6.0	---	6.2	6.3	5.9	11.7	12.3	11.7	11.8	4.4
C (μS/cm)	310	180	460	---	360	290	600	870	610	320	440	330
DO	---	---	---	---	---	---	---	---	---	---	---	10.59
TDS	320	300	400	---	310	340	580	860	610	280	430	320
HCO ₃	115	134	211	---	176	234	262	490	412	302	267	239
Ca	---	58.7	82.0	---	---	---	---	---	109	72.2	97.8	78.1
SO ₄	20	16	27	---	23	28	10	66	51	10	23	30
Cl	6	6	33	---	16	6	102	107	33	2	17	14
Mg	---	16.6	22.1	---	---	---	7	---	34.3	20.8	19.9	18.7
Na	---	3.5	9.5	---	---	---	---	---	23.0	2.2	6.1	5.4
NO ₃ -N	21	17	12	---	7.4	4.1	4.6	28	12	0.15	14	1.12
TOC	1.4	1.2	4.4	---	1.4	1.6	2.0	3.6	2.7	0.91	1.9	8.0
Fe	---	x	0.042	---	---	---	---	---	0.095	x	x	0.12
K	---	0.8	4.6	---	---	---	---	---	20.4	1.5	4.8	1.2
Total P	0.02	0.02	0.39	---	0.03	0.01	0.02	0.01	x	x	x	0.03
o-Phos	0.01PI	0.02	0.32PI	---	0.02	x	0.01	x	x	x	x	x
NH ₃ -N	x	x	0.8	---	0.1	x	x	0.2	1.2	x	x	0.03

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted; PI = possible interference

Chemical Composition Data of the Study Area, May 12-13, 2001

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.51	7.29	7.45	6.71	7.78	7.65	7.61	7.43	7.10	7.18	7.14	7.83
T (°C)	8.6	8.7	9.2	8.8	9.3	8.9	9.7	9.3	8.6	12.6	13.0	13.7
C (μS/cm)	420	470	470	2280	350	400	---	500	610	580	590	490
DO	0.98	2.36	2.55	0.29	0.71	8.20	1.67	2.24	0.35	0.32	0.55	8.40
NO ₃ -N	3.7	3.8	11	92	x	19	0.06	9.9	3.5	3.3	x	0.89
TOC	1.5	---	1.9	22	2.1	0.6	1.5	2.5	5.2	2.9	3.1	8.7
Total P	1.7	0.32	0.25	0.03	0.25	0.05	0.29	0.10	0.05	0.04	0.02	0.02
NH ₃ -N	x	x	x	4.7	0.02	x	0.04	x	0.1	x	0.12	0.05

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15
pH units	7.26	6.94	7.47	7.00	7.10	7.06	7.25	7.64	6.84	6.97	7.34	7.18
T (°C)	11.7	12.9	12.4	12.7	12.4	12.4	12.7	13.0	11.7	10.5	10.9	11.3
C (μS/cm)	420	390	460	500	330	460	410	790	1200	820	450	590
DO	---	---	---	---	---	---	---	---	---	---	---	---
NO ₃ -N	20	17	23	13	14	7.6	3.6	3.8	28	14	0.18	15
TOC	1.2	1.2	1.1	1.5	1.2	1.3	1.5	1.7	4.6	4.0	1.9	2.4
Total P	0.02	0.01	0.01	0.02	0.01	0.05	0.01	0.03	0.01	x	x	x
NH ₃ -N	x	x	x	x	x	x	x	x	x	1.4	x	x

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, June 9-10, 2001

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.55	7.40	7.52	6.76	7.94	7.66	7.67	7.43	7.13	7.31	7.37	7.84
T (°C)	11.3	10.8	11.8	11.4	11.5	10.6	11.4	9.7	9.7	13.3	10.7	15.6
C (μS/cm)	390	600	580	2120	440	350	360	510	580	550	510	500
DO	1.51	2.71	0.43	0.18	0.30	10.18	0.70	2.91	0.17	0.21	0.35	8.20
TDS	360	620	500	2100	480	240	380	380	410	460	500	410
HCO ₃	236	336	319	635	236	145	273	269	336	324	369	283
Ca	62.2	88.9	87.2	188	61.3	62.8	66.5	90.6	96.6	88.3	101	80.8
SO ₄	46	83	22	112	79	24	41	23	23	47	48	37
Cl	4	10	20	104	11	7	2	16	18	22	27	14
Mg	15.7	30.9	30.3	73	34.0	19.4	22.6	19.1	19.0	23.2	22.8	19.9
Na	6.9	4.5	3.7	44.6	3.4	2.5	3.9	3.9	4.8	13.0	10.7	5.0
NO ₃ -N	0.75	3.7	11	110	x	21	0.03	12	2.4	1.71	x	0.92
TOC	2.2	1.2	1.0	24	3.4	1.2	1.2	1.1	3.4	1.5	2.3	8.5
Fe	x	0.079	x	x	x	x	x	x	2.900	0.520	3.100	0.180
K	2.1	0.9	1.3	269	0.9	0.4	1.0	0.8	1.5	1.2	1.8	1.2
Total P	0.04	0.04	x	0.02	0.04	0.03	0.02	0.01	0.05	0.01	0.01	0.03
o-Phos	---	---	---	---	---	---	---	---	---	---	---	---
NH ₃ -N	0.08	x	x	4	x	x	0.02	x	0.14	0.04	0.12	0.04

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, June 9-10, 2001

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15
pH units	6.58	6.99	---	6.91	---	6.84	7.17	7.47	7.02	7.13	7.34	7.26
T (°C)	12.6	13.2	---	13.5	---	12.6	13.2	13.5	12.9	12.3	11.1	12.6
C (μS/cm)	280	380	---	410	---	360	430	600	1020	690	380	570
DO	---	---	---	---	---	---	---	---	---	---	---	---
TDS	280	310	---	390	---	320	340	730	910	690	300	410
HCO ₃	107	134	---	200	---	204	244	281	503	425	317	291
Ca	---	60.2	---	77.4	---	---	---	---	---	114	75.9	94.5
SO ₄	22	19	---	30	---	28	33	18	85	65	14	33
Cl	6	9	---	28	---	16	10	100	94	34	2	20
Mg	---	16.3	---	20.2	---	---	---	---	---	34.8	20.6	19.8
Na	---	3.0	---	7.	---	---	---	---	---	22.4	1.5	5.9
NO ₃ -N	17	18	---	13	---	4.6	4.7	10	28	14	0.18	12
TOC	1.4	1.6	---	2.7	---	1.5	2.3	1.8	4.0	3.6	---	2.0
Fe	---	x	---	0.031	---	---	---	---	---	x	x	x
K	---	1.2	---	3.9	---	---	---	---	---	20.3	1.6	4.5
Total P	0.02	0.01	---	0.12	---	0.03	0.01	0.02	0.01	x	x	x
o-Phos	---	---	---	---	---	---	---	---	---	---	---	---
NH ₃ -N	x	x	---	0.3	---	x	x	x	0.2	1.5	x	x

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, July 7-8, 2001

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.79	7.27	7.53	6.79	7.79	7.62	7.66	7.39	7.17	7.33	7.29	8.00
T (°C)	12.5	10.9	12.4	11.4	11.9	11.5	12.2	12.0	12.5	16.4	11.0	17.5
C (μS/cm)	410	580	600	2460	410	380	400	550	540	550	560	540
DO	0.57	1.83	1.53	0.38	0.19	8.85	0.74	2.38	0.04	0.16	0.34	7.39
NO ₃ -N	2.7	2.4	11	110	x	20	0.01	12	2.5	3.1	x	0.98
TOC	1.1	1.6	1.8	25	2.3	1.5	1.5	1.1	3.4	1.6	2.4	5.4
Total P	0.52	0.28	0.09	0.03	0.13	0.06	0.18	0.02	0.06	0.22	0.02	0.19
NH ₃ -N	x	x	x	5.8	0.01	x	0.05	x	0.2	x	0.13	0.03

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15
pH units	6.71	6.78	---	6.89	7.08	7.29	7.77	7.98	7.02	7.18	7.39	7.26
T (°C)	18.4	18.0	---	18.1	19.9	16.5	19.3	19.0	13.7	12.7	11.7	13.6
C (μS/cm)	350	340	---	500	490	550	490	860	1050	800	410	540
DO	---	---	---	---	---	---	---	---	---	---	---	---
NO ₃ -N	20	16	---	13	17	4.2	4.3	5.3	15	24	0.16	15
TOC	1.4	1.0	---	1.6	1.3	2.8	1.9	1.9	2.7	2.9	1.6	1.4
Total P	0.02	x	---	0.02	0.01	0.07	0.01	0.04	x	x	x	x
NH ₃ -N	x	x	---	x	x	0.5	x	x	1.9	0.2	x	0.2

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, September 8-9, 2001

	MW-1	MW-2	MW-3	MW-4	MW-5	MW-6	MW-7	MW-8	MW-9	MW-10	MW-11	SW-1
pH units	7.47	7.24	7.48	6.84	---	7.77	7.50	7.58	7.23	7.18	7.19	7.68
T (°C)	15.5	13.1	15.4	16.1	---	13.6	15.3	12.3	13.0	16.8	12.6	19.3
C (µS/cm)	390	630	670	2200	---	390	400	520	550	520	550	360
DO	2.98	3.01	1.97	0.53	---	8.92	1.16	6.51	0.95	0.83	0.55	6.73
TDS	330	520	580	1700	---	330	320	370	430	440	500	390
HCO ₃	175	387	318	779	---	150	270	223	325	322	363	265
Ca	58.5	98.0	101	172	---	65.5	66.8	83.6	96.1	93.2	105	80.8
SO ₄	34	80	16	119	---	24	40	18	25	48	50	38
Cl	4	9	56	145	---	6	2	13	18	14	29	17
Mg	11.9	33.4	32.5	73	---	19.6	22.3	17.3	18.4	23.8	22.2	21.6
Na	13.8	5.4	4.4	52.5	---	3.0	3.5	4.0	5.2	6.7	10.1	5.8
NO ₃ -N	13	1.15	10	79	---	18	x	16	3.7	1.83	x	0.79
TOC	1.3	1.1	1.6	27	---	0.8	1.9	0.8	3.5	1.5	2.3	4.4
Fe	x	x	x	x	---	x	65	x	3.0	0.81	3.8	0.033
K	3.4	1.1	1.6	322	---	0.5	1.2	0.9	1.7	1.3	2.0	1.6
Total P	0.04	0.05	0.01	0.08	---	0.04	0.32	0.03	0.08	0.08	0.02	0.01
o-Phos	---	---	---	---	---	---	---	---	---	---	---	---
NH ₃ -N	x	x	x	6	---	x	0.05	x	0.01	0.06	0.14	0.02

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

Chemical Composition Data of the Study Area, September 8-9, 2001

	TD-1	TD-2	TD-3	TD-4	TD-5	TD-6	TD-7	TD-8	MW-12	MW-13	MW-14	MW-15
pH units	6.85	---	---	6.82	---	7.38	---	7.15	7.01	7.16	7.43	7.33
T (°C)	18.5	---	---	20.5	---	21.4	---	20.3	16.4	15.5	11.7	15.2
C (μS/cm)	320	---	---	480	---	420	---	800	940	820	400	550
DO	---	---	---	---	---	---	---	---	---	---	---	---
TDS	260	---	---	400	---	360	---	670	810	700	320	400
HCO ₃	95	---	---	196	---	196	---	315	334	494	319	233
Ca	44.4	---	---	65.6	---	70.0	---	115	---	---	---	---
SO ₄	19	---	---	25	---	37	---	13	56	63	16	22
Cl	7	---	---	29	---	10	---	116	54	35	2	15
Mg	11.4	---	---	16.8	---	20.8	---	24.8	---	---	---	---
Na	2.0	---	---	7.7	---	3.6	---	20.6	---	---	---	---
NO ₃ -N	10	---	---	9.0	---	12	---	3.0	20	9.4	0.16	18
TOC	4.3	---	---	7.6	---	1.0	---	2.0	2.6	2.9	0.8	1.1
Fe	x	---	---	x	---	x	---	x	---	---	---	---
K	3.0	---	---	7.5	---	0.7	---	2.0	---	---	---	---
Total P	0.13	---	---	0.56	---	0.02	---	0.03	x	x	x	x
o-Phos	---	---	---	---	---	---	---	---	---	---	---	---
NH ₃ -N	x	---	---	0.3	---	x	---	x	0.4	2.2	x	x

dashes (---) indicate no measurements made; x = below detection limits; units are in mg/L unless otherwise noted

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