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NITROGEN TRANSPORT AND SPECIATION IN A
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NITROGEN TRANSPORT AND SPECIATION IN A WATERSHED IN SOUTHWEST MICHIGAN

By

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ABSTRACT

NITROGEN TRANSPORT AND SPECIATION IN A WATERSHED IN SOUTHWESTERN MICHIGAN

By

Stephen Scranton Aichele

This study investigates the transformations and transport pathways of nitrogen in a sandy, agricultural watershed in southwestern Michigan, with the intent of better understanding the environmental fate of nitrogen. The study site is a small (<20 ha), rural watershed, containing an organic wetland and a small tributary stream. Water entering the wetland has been observed to contain between one and two ppm nitrate, while water leaving the wetland has between 5 and 8 ppm nitrate.

Analysis of samples from the upland soils discovered no serious overloading of nitrogen. Profiling inside the wetland indicated that while mixing was occurring, clear aerobic and anaerobic zones exist. Ammonium was found in many of the deeper (anaerobic) wetland piezometers. Residual organic matter within the wetland is probably mineralizing in an anaerobic environment to form ammonium, which nitrifies near the water's surface. This site may continue to release nitrate into the outflow stream for decades.

ACKNOWLEDGMENTS

I would like to take this opportunity to recognize a few of the people who have encouraged and supported me both in conducting the research and in writing this thesis.

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Joe Ervin, who has always been there to discuss odd findings, in the field and in the lab.

Finally, last but by no means least, my fiancé, Tracy Szathmary, who spent more early mornings in the car to Cass County and more sub-freezing days knee deep in water than anyone has a right to ask. Nearly as important, she has helped me keep my life together for the last three years. I only hope I can do as good a job for her as she completes her thesis.

TABLE OF CONTENTS

CHAPTER 4

CHAPTER 5

LIST OF FIGURES

LIST OF TABLES

Chapter 1

INTRODUCTION

Our surroundings abound in nitrogen. Nitrogen is the most common element in our atmosphere, and one of the most common in the earth's crust. Nitrogen is also a vital nutrient in cultivated agriculture, a crucial component of animal proteins, and a minor constituent of livestock waste. One specific form of mineral nitrogen, the oxidized species nitrate (NO_3^-), poses a problem because it is both highly soluble and extremely mobile in the surficial environment. Elevated concentrations of nitrate in drinking water have been shown to cause infantile methemoglobinemia (blue-baby syndrome), and environmental contamination by nitrogen is a major threat to surface water systems, resulting in eutrophication and, potentially, fish kills. Increasingly, farmers and rural communities, both in the United States and throughout the world, have realized the need to control this common, essential, and potentially harmful nutrient.

One such project, intended both to enhance our understanding of nitrogen and to educate the community on the extent and control of nitrogen pollution, has been carried out by the Michigan State University Institute for Water Research, in conjunction with the Geology

Department of Western Michigan University and several other groups. These organizations have been active in recent years studying the role and fate of nitrogen in the environment, specifically in the Donnell Lake watershed of Cass County, in southwestern Michigan. The focus of this research has been the impact of agricultural waste on surface and groundwater quality. The research has been conducted both at the watershed scale (approximately 52 km^2) and at the sub-watershed scale (less than 2 km^2). While this work has been helpful in researching nitrogen cycling, and is vital to educating the community, several apparent anomalies have been discovered which were not within the scope of the larger project. A better understanding of these anomalies would certainly help with the Donnell Lake project, and may well add to the study of the environmental fate of nitrogen.

One such anomaly occurs at a small wetland west of Robbins Lake Road in Section 33, Cass County, MI, approximately 3 km (2 miles) west of Jones (Figure 1). The wetland lies upstream (east) of Donnell Lake proper, and is approximately 2.5 ha (5 acres) in area. The property is owned by William White, who has been very helpful and cooperative in both this specific research and in the larger project. Mr. White has been raising swine on the property, and uses the fields adjoining the property to dispose of manure, provide pasture area for the swine, and to grow corn, which is used as swine feed. The wetland was monitored on an irregular basis by the Institute staff as they sampled up the watershed from Donnell Lake. Despite the fact that Mr. White modified his management practices on the advice of these researchers, the quality of the water leaving the small watershed has not improved. This situation contrasts with several other similar sites in the Donnell Lake watershed where modifications in management practices *have*

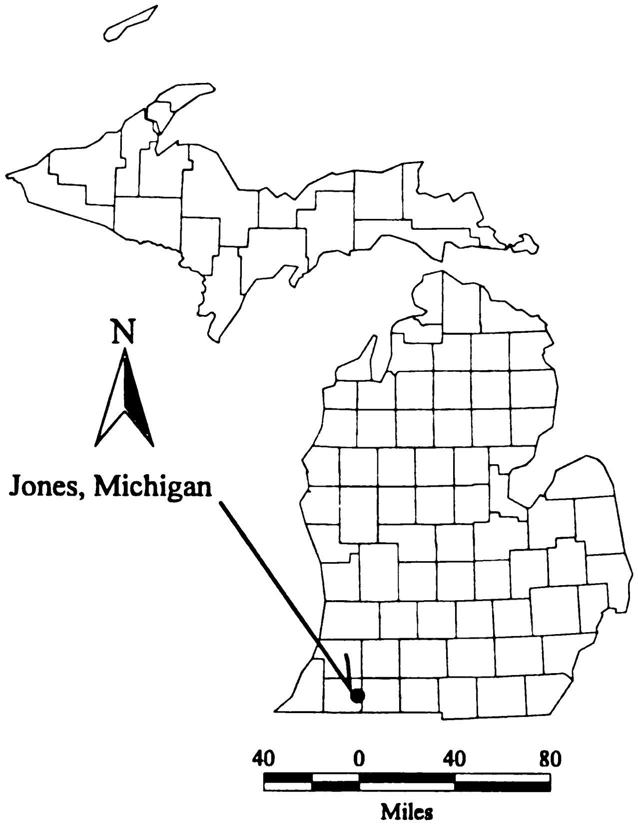

Figure 1: Location of Jones in southwestern Michigan.

substantially improved surface and ground water quality within a similar time frame. In fact, despite increases in discharge through the length of the watershed, nitrate levels in the wetland have been observed to increase from approximately 1 part per million (ppm) at the head of the wetland to more than 5 ppm at the outflow stream. In summary, as water flows through this small sub-watershed, the nitrate concentration increases, even though the potentially diluting effects of increased discharge also occur in this reach. The increasing nitrate levels in the watershed contrast with our understanding of nitrate behavior. Organic wetlands are commonly thought to be nutrient sinks (Johnston, 1991), yet this one appears to be *producing* nitrate.

Problem Statement

The observed spatial patterns of nitrate in the wetland conflict with the general belief that bog/marsh wetlands are nutrient sinks. These patterns also contrast with patterns observed elsewhere in the Donnell Lake area, in which modified management practices have positively impacted water quality. The intent of this study is to determine in more detail the spatial patterns of nitrate in the wetland and the surrounding up-slope area, and address the question of why these patterns exist. With this problem in mind, the purpose of this study is to determine the sources of the anomalous nitrate in the wetland, with the intent to identify a remediation strategy.

Justification

This anomalous nitrogen occurrence provides an opportunity to further our understanding of the behavior of nitrogen in the environment, both for the larger good and for the direct purpose of guiding remediation efforts both at this site and at others elsewhere. Nitrogen contamination is a significant problem in southwestern Michigan, where the surficial sands and gravels serve as the only source of potable domestic well water.

Loosely stated, the objective of this study is to determine what is causing the increasing concentration of NO_3^- in the stream despite its increasing discharge. More specifically, I endeavor to separate hypothesized sources of nitrogen as a way of isolating a source or mechanism. In brief, there are three ways nitrogen could be entering the wetland area: (1) through storm driven overland flow, (2) through the existing stream channel network, or (3) through shallow ground water flow. Each of these pathways will be isolated and observed for any spatial correlation to the occurrence of nitrate in the stream. Further, samples of soils in the surrounding fields will be collected and analyzed to assess whether the modification in management practices has had the effect of removing excess nitrogen from the soil. Because nitrogen speciation is rapid and crucial to the understanding of the movement of nitrogen in the environment, both the oxidized (NO_3^-)and reduced (NH_4^+) forms of mineral nitrogen will be monitored.

Site description

The site is approximately 15 ha in area, on the west side of Robbins Lake Road in SW ¼, NE ¼, SW ¼, Section 33, Tier 6 South, Range 13 West, Cass County, Michigan (Figure 2).

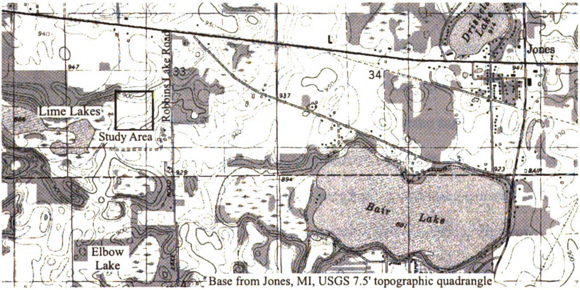

Figure 2: Detail map of study area relative to Lime Lakes and Jones, MI.

The topography of the region is the product of deposition of glacial outwash by rapidly melting Laurentide ice sheet. The resulting sand and gravel is very porous and highly permeable, and is the drinking water aquifer for the majority of people in the area, through individual domestic wells. The area immediately surrounding the study site, and encompassing Donnell Lake, Lime Lakes, and Bair Lake, is the result of sediment deposited in contact with stagnant ice, with subsequent gravity slumping (Leverett, 1912; Leverett and Taylor, 1915; Ervin et al. 1996; Kehew, personal communication, 1998). This slumping 16,000 years ago resulted in the incongruously rough topography to the east of Lime Lakes, amidst what is otherwise smooth to gently rolling outwash plain. Soils surrounding the study site are generally coarse-textured. Bedrock is as much as 45m (150 feet) below the land surface (Kehew, 1996).

Despite the post-depositional slumping, and subsequent reworking by environmental processes over the last 15,000 years, surficial materials are entirely consistent with the outwash setting. Two soils are dominant at the Lime Lakes study site, the Kalamazoo loam (fine-loamy, mixed, mesic Typic Hapludalf) and the Oshtemo sandy loam (coarse-loamy, mixed, mesic Typic Hapludalf), with a modest area of Brady sandy loam (Coarse-loamy, mixed, mesic Aquollic Hapludalfs) in the area near the tributary stream feeding into the wetland from the east (USDA, Soil Conservation Service, 1991). Horizons within the Kalamazoo series are Ap, Bt1, Bt2, Bt3, Bt4, 2BC, 2C1, and 2C2. Within the Oshtemo series horizons are similar : Ap, Bt1, Bt2, Bt3, 2BC, and 2C. Typical horizons for the Brady soils are Ap, E, Bt1, Bt2, BC, and 2C. The wetland itself is mapped as Adrian muck, which typically has Oa1, Oa2, C1, C2 and C3 horizons (USDA, Soil

Conservation Service, 1991). Both the Kalamazoo and Oshtemo soils are very sandy, with little development below 1m (USDA, Natural Resource Conservation Service, 1992; 1996). Profile descriptions from the Soil survey of Cass County can be found in Appendix A. The land immediately adjoining the wetland has been removed from active agriculture, and on the south side of the wetland provides a buffer of approximately 15m between the agricultural land and the wetland. Beyond the buffer on the south side, half of the land in the watershed is planted in corn, half used as pasture. On the north side, because of a steep slope, the land has been left as grass for as much as 90m (300 ft) uphill from the edge of the wetland. Beyond the grass buffer is a field of corn (Figure 3).

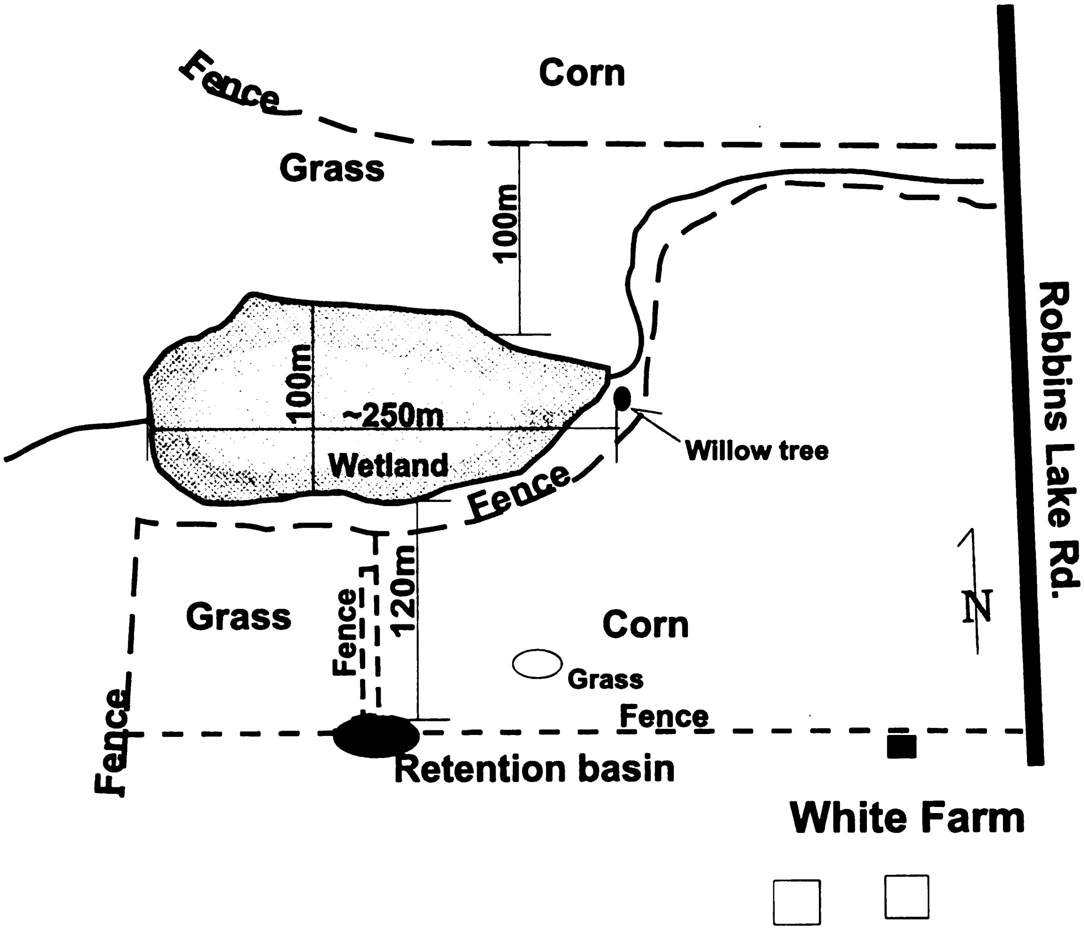

Figure 3: Diagram of the study site.

Chapter 2

REVIEW OF EXISTING LITERATURE

Nitrogen has been a subject of research in agronomy and other sciences for more than a century (Paul and Clark, 1989). Consequently, a vast body of literature exists, with topics ranging from nitrogen as a fertilizer to its role as an atmospheric pollutant. Only a small portion of this literature is pertinent to this discussion. Much of the information presented below represents a summation or combination of well-known agronomic information for application to hydrology and water quality. Consequently, it is important to recognize that the relatively few authors cited have built upon the work of literally hundreds of researchers working over a century or more.

Distribution of Nitrogen Pollution

Nitrate (NO_3^-), the oxidized mineral form of nitrogen, is the most widespread contaminant of drinking water in the world (Freeze and Cherry, 1979). Nitrate pollution is most commonly found in either coarse-textured sediments or near-surface fractured rock aquifers, especially when the dominant regional land use is either row cropping or livestock (Spalding and Exner, 1991). Consequently, NO_3^- contamination impacts nearly every state in the contiguous United States, as well as many countries in Europe and elsewhere (Fried, 1991).

A survey by Madison and Brunett (1985), based on data compiled in the U.S. Geological Survey's (USGS) Water Storage and Retrieval System (WATSTORE), reported NO_3^- in groundwater in broad regions of the lower Susquehanna Valley and Delmarva Peninsula, the Plains states of Texas, Oklahoma, Kansas, Nebraska, Iowa, the Dakotas, the Great Lakes states of Minnesota and Wisconsin, as well as the Southern California and Arizona irrigated agricultural regions. Madison and Brunett (1985) conceded that because much of the data in WATSTORE was collected for specific studies, it is neither spatially, temporally, nor vertically representative. It is, however, an accounting of recorded observations.

Lee and Nielsen (1989), building on Madison and Brunett's work, combined data from WATSTORE with vulnerability model information and chemical use data to derive a map of the potential for non-point source nitrate and pesticide contamination. This map was significant in that the eastern Corn Belt states of Ohio, Indiana, and Illinois were considered vulnerable to contamination.

Spalding and Exner (1991) referred to the difficulties of mapping NO_3^- vulnerability in glaciated terrain, such as the Great Lakes region. Several researchers have made attempts to identify areas of either vulnerability or confirmed contamination in the Great Lakes. Kittleson (1987) demonstrated that the extent of observed NO_3^- contamination in the

Lower Peninsula of Michigan had increased based on comparisons of data collected in the period 1933-1970 with data from 1975-1984. Kittleson based his research on analyses of public water supply wells obtained from the Michigan Department of Public Health. Lusch et al. (1992) produced a map of potentially sensitive areas in the state of Michigan based on properties of soils and glacial drift lithology. The results correlate remarkably well with Kittleson's areas of known contamination, considering the different approaches used. Three recurrent factors seem to be present in nearly all cases: 1) highly permeable soils, 2) highly transmissive glacial drift aquifers, and 3) intensive agricultural landuses.

The Institute of Water Research at Michigan State University has been involved in an ongoing study of agricultural land use impacts in the Donnell Lake watershed, in east-central Cass County, Michigan. In describing the geological characteristics of the region, Ervin et al. (1994) also cited the glacial history of the area as making the groundwater supplies of the region particularly susceptible to contamination by surface sources. The region around Donnell Lake has all three of the risk factors cited above.

The Nitrogen Cycle

Nitrogen can be found in the atmosphere, soils, and nearly all living tissue, from microbes to plants to humans. Transfers of nitrogen between these reservoirs is called the nitrogen cycle, first described by Löhnis in 1913 (Paul and Clark, 1989). In brief, the cycle proceeds as a result of nitrogen fixation by leguminous vegetation, which creates a reserve of nitrogen in the soil (Behnke, 1975). This nitrogen could be taken up by non-leguminous plants, which could then be consumed by animals. Plants and animals use the nitrogen to construct proteins, most of which are eventually returned to the environment through either excretia or the ultimate decomposition of the animal tissue. At this point nitrogen is once again in the mineral form, and is accessible for plants (Behnke, 1975). Some additional mineral nitrogen is input to the terrestrial and biotic system as a result of precipitation, but this typically amounts to less than 18 kg/ha (20 lbs/acre) annually (Cummings, 1984). The complexities of the nitrogen cycle are described elsewhere (Paul and Clark, 1989, and Keeney, 1986, are two particularly good ones) and will not be repeated here. Only the specific transformations relevant to the project will be described in detail. A diagram, fashioned after that found in Freeze and Cherry (1979, p. 414), is included as Figure 4.

The nitrogen cycle, as applied to the study site, can be traced as follows. Feed is provided to swine, primarily in a confined feeding facility, but also as corn and fodder in the fields. While some of this feed was grown on site the previous season, much of it is imported into the system as commercial feeds. The swine probably excrete waste at a rate of between 3.2 - 3.6 kg/day (Taiganides and Hazen, 1966; Scholz, 1971; Taiganides and Stroshine, 1971). Of this, roughly 63% is excreted as feces and 37% as urine, on a weight basis (Azevedo and Stout, 1974). Between 85% and 90% of the excreta is water, leaving between 0.45 and 0.7 kg/day/swine of “dry matter” (Taiganides and Hazen, 1966; Scholz, 1971; Taiganides and Stroshine, 1971; Conrad and Mayrose, 1971). Various authors have found swine manure to contain between 2.0% (Hileman, 1967) and 4.6%

(Salter and Schollenberger, 1939) nitrogen, on a dry weight basis. Thus, if we assume each hog produces 0.57 kg/day of dry matter (researchers report values between 0.45 and 0.7 kg/day), with an N content of 2.5%, one hog will produce 0.14 kg-N/day, or nearly 52 kg of N per year. This nitrogen, along with roughly 180 kg/year of other dry matter waste, must be disposed of in some manner. One very common and long practiced method is to apply the manure waste to nearby fields.

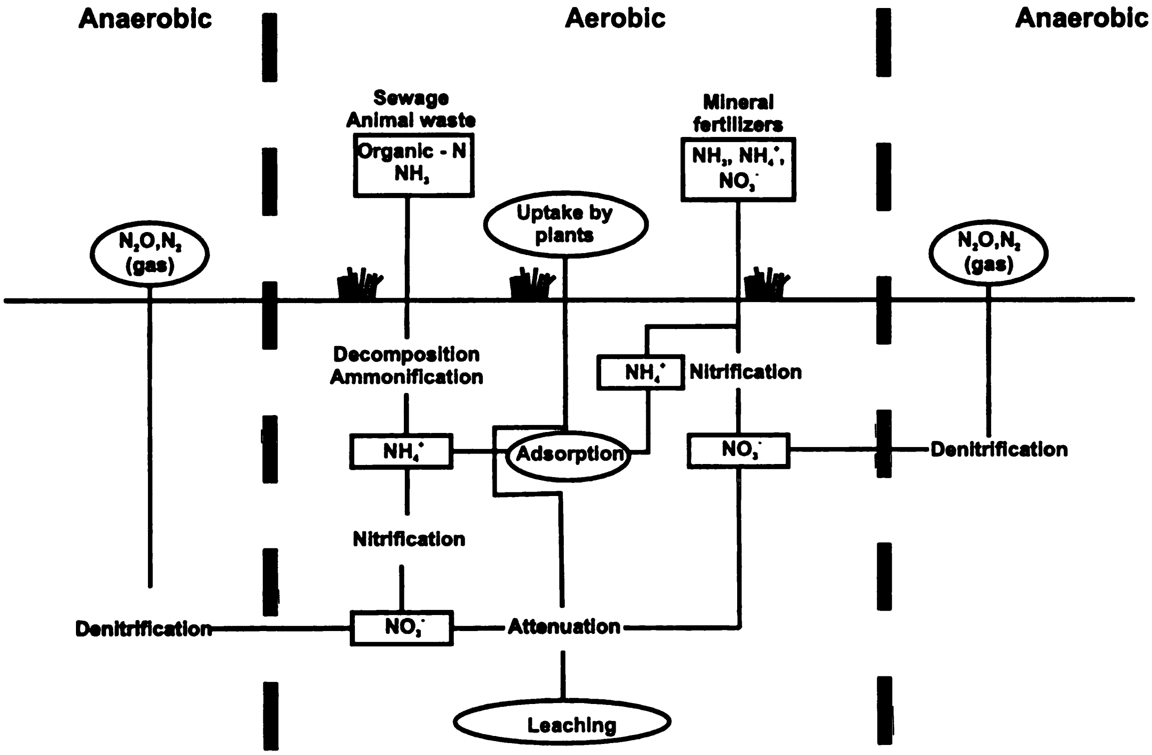

Figure 4: The nitrogen cycle.

Returning the manure to the soil increases the overall fertility of the soil, because manure is also rich in phosphorus, potassium, and is a source of micronutrients. However, in modern confined feeding situations, often the amount of manure fertilizer available far exceeds the fertilizer needs of even the most demanding crops (Azevedo and Stout, 1974). Corn, the crop usually grown on the site and one of the most demanding crops in terms of nitrogen consumption, can rarely incorporate more than 135 kg-N/ha. At this rate, one hectare of land could adequately utilize the manure of only 2.6 swine, based on the numbers given above.

Plants are not able to directly incorporate the nitrogen found in manure. The nutrients in the excreta are typically organic compounds, with nitrogen usually in the form of urea. This organic-N must first undergo ammonification, a microbial process in which heterotrophs separate the ammonium groups from the carbon and oxygen in the urea. This results in mineral ammonium, NH_4^+. Though the ion is positively charged, the N atom is in the reduced state.

Because of the temperate climate and coarse-textured, oxygen-rich soil conditions commonly found in southwest Michigan, the bulk of manure applied to fields in southern Michigan undergoes both ammonification and nitrification, the oxidation of the reduced ammonium ion (NH_4^+) to nitrite (NO_2^-) and then to nitrate (NO_3^-), often within a period of two weeks or less (Ellis, personal communication, 1996). Gold et al. (1990) found that NO_3^- accounted for between 83% and 96% of the mineral nitrogen in their samples, from similar glacial outwash deposits in climatically similar Rhode Island. Again, this is a microbially-governed process and will only occur in an oxidizing, aerobic environment. The overall equation for the nitrification process is:

$$NH_4^+ + 1^1/_2\,O_2 \overset{6e}{=>} NO_2^- + H_2O + 2H^+$$

(Keeney, 1986)

This reaction yields energy for microbial growth. Some of the chemautotrophic bacteria identified as utilizing this reaction for energy in non-marine environments are *Nitrosomonas europaea* (in soil, water, and sewage), *Nitrosospira briensis* (in soil), *Nitrosococcus mobilis* (in soil), and *Nitrosovibrio tenuis* (in soil) (Paul and Clark, 1989). The additional oxidation step from nitrite (NO_2^-) to nitrate (NO_3^-) is commonly represented as:

$$NO_2^- + ½\,O_2 \overset{2e}{=>} NO_3^-$$

(Keeney, 1986)

Again, this reaction yields some energy for microbial growth, though less (approximately 27%) than the NH_4^+ to NO_2^- oxidation. As a result, the microbes utilizing this reaction as an energy source must be extremely efficient to survive (Keeney, 1986). This explains why NO_2^- seldom occurs in high concentrations in soils or waters. The two species known to utilize this reaction in non-marine environments are *Nitrobacter agilis* (in soil and water) and *Nitrobacter winogradsyi* (in soil);(Paul and Clark, 1989). The reversal of this process within the human digestive tract is responsible for most of the health risks associated with nitrogen pollution (Crespi and Ramazotti, 1991).

Ammonium (NH_4^+), because it is a positively charged cation, can form an electrochemical bond with negatively charged particles in the soil, primarily clay minerals and organic molecules. Negatively charged particles provide cation exchange sites, and the ability of a soil to retain cations is termed its cation exchange capacity (CEC). The CEC of the soils in the study area is very low (USDA, Natural Resource Conservation Service, 1996), due to comparatively low clay and organic matter contents. Both CEC and water retention generally decrease with depth. Further, because of the high sand content and general climatic circumstances of the study site, the upland areas are both aerobic and oxidizing, resulting in the rapid oxidation of NH_4^+ to NO_2^- and eventually NO_3^-.

The conversion from NH_4^+ to NO_3^- is essentially non-reversible. While a limited return path exists in the incorporation of nitrogen into microbial biomass, the process is a detour at best, because this nitrogen is eventually returned through decomposition of the microbes. Tiedje (1988) has documented the existence of microbes capable of dissimilatory nitrate reduction to ammonium (DNRA) under extremely anaerobic conditions. D'Angelo and Reddy (1993) have found similar bacteria in lake sediments in Florida. Both of these studies are somewhat suspect because of the problem of transporting NO_3^- into a highly reducing environment. In environmental conditions, denitrifying bacteria at the aerobic/anaerobic interface would reduce the NO_3^- to N_2O or N_2 before DNRA could occur. Thus, under nearly all environmental circumstances, when nitrate is exposed to reducing conditions it will be reduced to either N_2O or N_2, both of which are eventually lost to the atmosphere as gas. The reduction of NO_3^- is known as denitrification, in which the NO_3^- ion is used as a terminal electron acceptor, essentially taking the role of oxygen in microbial respiration under microaerobic or anaerobic conditions, assuming adequate organic carbon for respiration and microbial growth (Keeney, 1986). Over one dozen genera of denitrifying bacteria are known, and they are present in most soil and aquatic environments (Keeney, 1986). The generally accepted pathway for denitrification, outlined by Keeney (1986) and others (Paul and Clark, 1989; Tiedje, 1988; Burt and Haycock, 1991), and culminating in either N_2O or N_2 release is:

$$NO_3^- \Rightarrow NO_2^- + e^- \Rightarrow NO + O^- \Rightarrow N_2O \Rightarrow N_2$$

Because NO_3^- is an anion i.e., negatively charged, and the bulk of the charged particles within the soil matrix are negatively charged, there is little potential for bonding of NO_3^- ions to the soil, except to organic matter. As a result, NO_3^- ions are very likely to be translocated or “leached” by infiltrating water (Brady, 1974; Freeze and Cherry, 1982). Kehew et al. (1996) working approximately 45 km (30 miles) north of the study site, but in a very similar geologic environment, described the conditions of land use surrounding this site. Their description included livestock pens and land applied fertilizer in excess of 180 kg/ha (200 lbs/acre). They go on to state “Nitrogen applications, coupled with a shallow water table and permeable soils, make ground-water contamination a virtual certainty (p. 498).”

Nitrogen Transport in the Saturated and Unsaturated Zones

Transport of NO_3^- and other soluble constituents in the saturated zone has been well documented in both general hydrology texts (Freeze and Cherry, 1982; Fetter, 1994), and more technically specific literature (e.g., Hillel, 1982; Kehew, 1996). Water flow through saturated porous media is based on the hydraulic head difference between two points and the distance between those two points. The rate of flow is determined by the head gradient and the transmissivity of the media.

Solute transport and water flow in the unsaturated zone is highly variable. Because NO_3^- is a soluble anion, with little capacity to adsorb to soil particles, transport of NO_3^- is directly dependent on water flow. Hillel (1980) wrote the seminal treatise on unsaturated zone flow. According to Hillel, flow in soil is governed by two forces, suction and gravity. The ability of a soil to accept moisture from the land surface is based on the permeability of the surface layer, or its *infiltrability*. When the infiltrability of the soil is exceeded, evidenced by ponding, both suction and gravity act to draw water into the soil. Because water held within the unsaturated portion of the soil column is held under tension, the ponded water forms a reservoir for capillary transport of water, just as the water table serves as a source of water for capillary rise under non-infiltration conditions. Thus the tensile forces of water in underlying but connected pore spaces act to "suck" the water at the surface down into the soil column. The effect of this force decreases with distance from the source, and at some depth it becomes negligible.

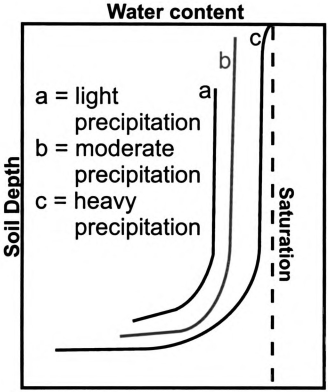

Figure 5: Water content breakthrough curves (after Hillel, 1980).

When the infiltrability of the soil is not exceeded, gravity acts alone to move water into the soil column. As the field capacity of each individual pore is exceeded, water begins to flow out of that pore and into a deeper pore. However, at some point the influx of water at the soil surface ceases, the progression of water through the column, or wetting front, halts. This relationship, in the form of breakthrough curves, was illustrated by Hillel (Figure 5). Only when the wetting front reaches to the saturated zone does recharge, and consequently contamination by leached NO_3^-, occur. In all other cases, NO_3^- is attenuated with water held within the soil column.

Nitrogen-related problems

Nitrogen pollution has been identified with an assortment of environmental maladies; including eutrophication of surface water, depletion of stratospheric ozone by N_2O released during denitrification, and an assortment of human health problems, including birth defects, cancer, nervous system impairments, and infantile methemoglobinemia ("blue baby syndrome"). While all are important, the issues relating to eutrophication and human health are the most significant within the context of the larger Donnell Lake study (Ervin et al., 1994).

EUTROPHICATION

The processes involved in eutrophication have been well-known for several decades and do not need to be discussed in detail here. For further information, the reader is referred to Beeton's (1969) assessment of eutrophication in the Great Lakes, Henderson-Sellers' (1987) book detailing both the process and case studies, or D'Angelo and Reddy's (1993) article describing the detailed chemistry of the process in a specific lake. Finally, Welch (1980) described in detail the multiple effects of wastewater inputs to hydrologic systems, including farm run-off.

While eutrophication is a natural and inevitable process, the progression of a lake or lacustrine system from oligotrophic (nutrient poor) through mesotrophic to eutrophic (nutrient rich) can be greatly accelerated by the influences of humans on the landscape (Bolsenga and Herdendorf, 1993). In summary, increased nutrient loading in the geo-hydrologic system stimulates growth of biomass in the water body. If the eutrophication is caused by increased inputs of raw waste, both microbial and vegetable populations will grow. Because the raw waste provides a good source of organic carbon, microbial populations will attempt to expand to the limit of this new food supply. These microbes consume both organic carbon and oxygen, resulting in lower dissolved oxygen levels and more nutrients available in ionic forms, such as NH_4^+.

Whether the input source is raw waste or leached ions, the increased concentrations of ionic nutrients in the water body then may stimulate plant growth. Plants require oxygen to respire, both day and night. While the plants themselves produce excess oxygen during the daytime as a byproduct of photosynthesis, during the night respiration must continue, and the plants further deplete dissolved oxygen reserves that are also necessary to aquatic animal life. This depletion can result in such severe shortages of dissolved oxygen (DO) from that certain aquatic animal species disappear from the ecosystem. Lakes and streams that are experiencing eutrophication are often so congested with vegetable matter that they are not considered desirable for recreational use. Human land use changes over the last 200 years, particularly as a result of agricultural practices, have been responsible for much of the greatly increased nutrient loading to rivers and lakes (Bolsenga and Herdendorf, 1993)

HEALTH ISSUES

Nitrogen, specifically NO_3^-, has long been linked to infantile methemoglobinemia (Comly, 1945). Methemoglobinemia (blue baby syndrome) occurs when an oxidizing agent, NO_2^- in this case, oxidizes the iron in hemoglobin from ferrous iron to its ferric form (Fe^{3+}) (Mirvish, 1991). This oxidation by NO_2^- reduces the oxygen carrying capacity of the hemoglobin (now methemoglobin) and results in cyanosis (blue blood) and anoxia (lack of oxygen in the blood). While NO_2^- is rare in nature, NO_3^- can be reduced in the digestive tract to NO_2^- (Crespi and Ramazzotti, 1991; Keeney and Follett, 1991). Susceptibility to methemoglobinemia varies, however, based on body mass, age, and diet. Infants under 3 to 6 months of age, particularly those not yet eating solid food, are most at risk. This is because 1) infantile hemoglobin is more susceptible to oxidation by nitrite than adult hemoglobin, 2) infants consume more water in relation to their body weight than do adults, and 3) the activity of the enzyme system that reduces methemoglobin is lower in infants than in adults (Keeney and Follett, 1991). For this reason, the U.S. Environmental Protection Agency (USEPA) has set a Maximum Concentration Limit (MCL) of 10 ppm for drinking water (USEPA, 1994).

Several authors (Keeney, 1986; Keeney and Follett, 1991; Moller and Forman,1991; Crespi and Ramazzotti, 1991) have accepted a correlative relationship between NO_3^- consumption and various forms of cancer, usually gastric cancer. Nitrate consumed in food or water is reduced in the acidic environment of the stomach to form NO_2^-, which then may bond to naturally produced amines in the digestive tract to form nitrosamines, which have been demonstrated to be carcinogenic (Crespi and Ramazotti, 1991). While this has only been demonstrated in laboratory animals to date, the pathway exists in humans as well.

Other Studies

Several recent studies in the Upper Midwest, the glaciated Northeast, and the coastal plain deposits of the Chesapeake Bay address similar issues of nitrogen transformation and transport in unconsolidated or weakly consolidated material. Staver and Brinsfield (1990) studied the temporal patterns of NO_3^- availability in the soil and NO_3^- leaching over the course of a year. They discovered that the highest reserve of soil nitrogen was present toward the end of the growing season, from approximately September to January. Presumably this is the result of decreased crop uptake late in the season followed by harvesting of the crop, which eliminates its nitrogen uptake.

Staver (1994) attempted to quantify advective transport of NO_3^- in three phases: 1) transport into the permanently saturated portion of the profile, 2) net transport into the unconfined aquifer in the transient/unsaturated region of the soil profile, and 3) transport of NO_3^- from the root zone into the vadose zone. This work is significant primarily for the methodology employed in sampling shallow groundwater through manually installed PVC piezometers. This method significantly reduced the equipment cost for monitoring, resulting in a more extensive network of sampling sites. Using PVC in place of more conventional metal peizometers also removes some of the potential for electrochemical modification of the oxidation-reduction conditions within the peizometer. Several other aspects, such as the use of horizontal piezometers in the place of conventional lysimeters, are intriguing, but were not employed in my study. Staver's finding that the rye cover crop substantially decreased the pool of available NO_3^- in the soil is also of interest, because while no cover crop was used in the Cass County study area, several samples were obtained from land permanently covered in rye grass.

Gold et al. (1990) studied NO_3^- losses to groundwater in different land-use areas with well drained soils, overlying highly permeable unconfined glacial outwash aquifers, near Kingston, Rhode Island. This study found that between 83% and 96% of the inorganic nitrogen present in the percolate was present in the oxidized form of NO_3^-, as opposed to NH_4^+. This is significant because of the hydrologic similarities between their Kingston study sites and the Cass County site. Six different land-use scenarios were studied, including urea-fertilized corn, manure-fertilized corn, septic systems, and fertilized home lawns. Manure-fertilized corn regularly produced the most NO_3^- rich leachate, excluding septic systems.

Kehew et al. (1996), working in glacial deposits approximately 45 km (30 miles) northeast of the Cass County study site, found ample NO_3^- loading in conjunction with confined feeding operations in that area. They also discovered that shallow groundwater within the outwash aquifer was interacting with lakes and other surface water, thus the chemistry of water in the aquifer was highly dependent on the position of the sample point relative to a lake or wetland. Generally, waters down-gradient from lakes and wetlands were found to have both more reducing conditions and high iron concentrations, relative to waters upgradient from the lake or wetland. While they made no inferences as to the cause of this phenomenon, the facts are consistent with very active microbial population in the lakes and wetlands. However, in this sort of situation, one would typically expect denitrification to occur in the wetlands coincident with the decrease in redox potential.

Chapter 3

METHODS

Field Methods

SURVEYING

The first field task, to facilitate finding the same sampling locations later, involved establishing a visible and robust spatial referencing system on the site. Because there were no adequate cultural reference marks on site, I designed my own system using a Brunton pocket transit, a tripod, a hip-chain and the assistance of friends. Beginning with an initial point at the eastern end of the wetland, where the small tributary stream ceases to be channeled, I constructed one north-south transect that extended to the northernmost and southernmost ends of the wetland, approximately 50m (165 ft) in each direction. The initial base point is 6m (20 ft) NNE of the trunk of the large willow tree on the site. Using this transect as the eastern baseline, I surveyed two additional transects perpendicular (due west) from the endpoints of the first transect, to a distance of 240m (800 ft). These two parallel east-west transects were marked every 30m (100 ft) with 2m (6 ft) wooden stakes painted orange, to define eight total north-south transects, easily discernible from anywhere within the site. The transects were numbered from east to west, from one to eight. This ladder configuration, with stringers running east-west and rungs running north-south, formed the basis of the subsequent sampling and spatial referencing scheme (Figure 6).

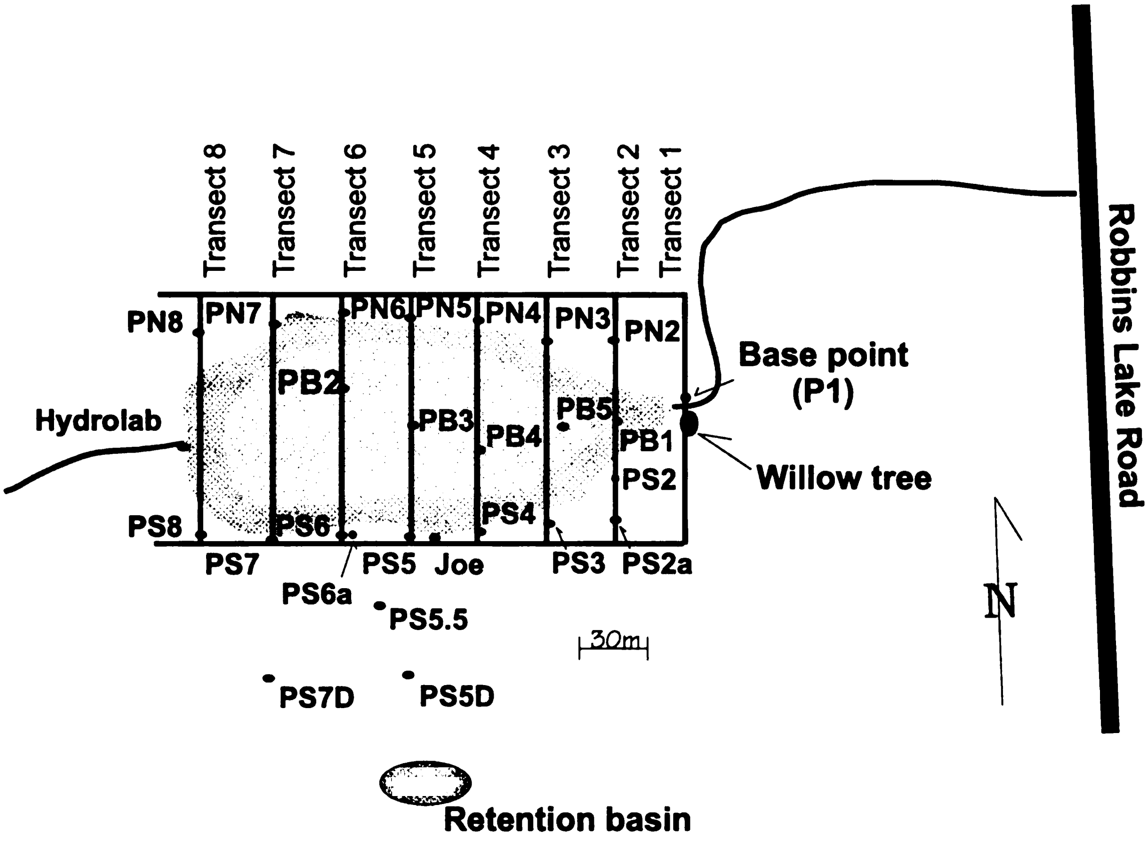

Figure 6: Basic spatial referencing system used at the site.

WATER SAMPLING

In order to monitor groundwater moving into the wetland, I positioned piezometers on both sides of the wetland. The edge of the wetland was, for the purposes of this study, determined to be where mineral soils give way to mucks. Groundwater piezometers were located on the north-south transects (rungs) at the edge of the wetland, with one located at the base point near the willow tree (Figure 7). I installed piezometers every 30m (100 ft) over a distance of 210m (700 ft) on both the north and south sides of the wetland.

To install the groundwater piezometers, I used a 10cm (3 inch) diameter, 2m (6 ft) long bucket auger. Groundwater piezometers were initially located only at the intersections of the east-west transects and the north-south transects. A soil sample was collected every 30cm (1ft) vertically until the soil became saturated, with the first sample at a depth of 30cm (1ft). In most instances, the soil became saturated within a meter (3 ft) of the

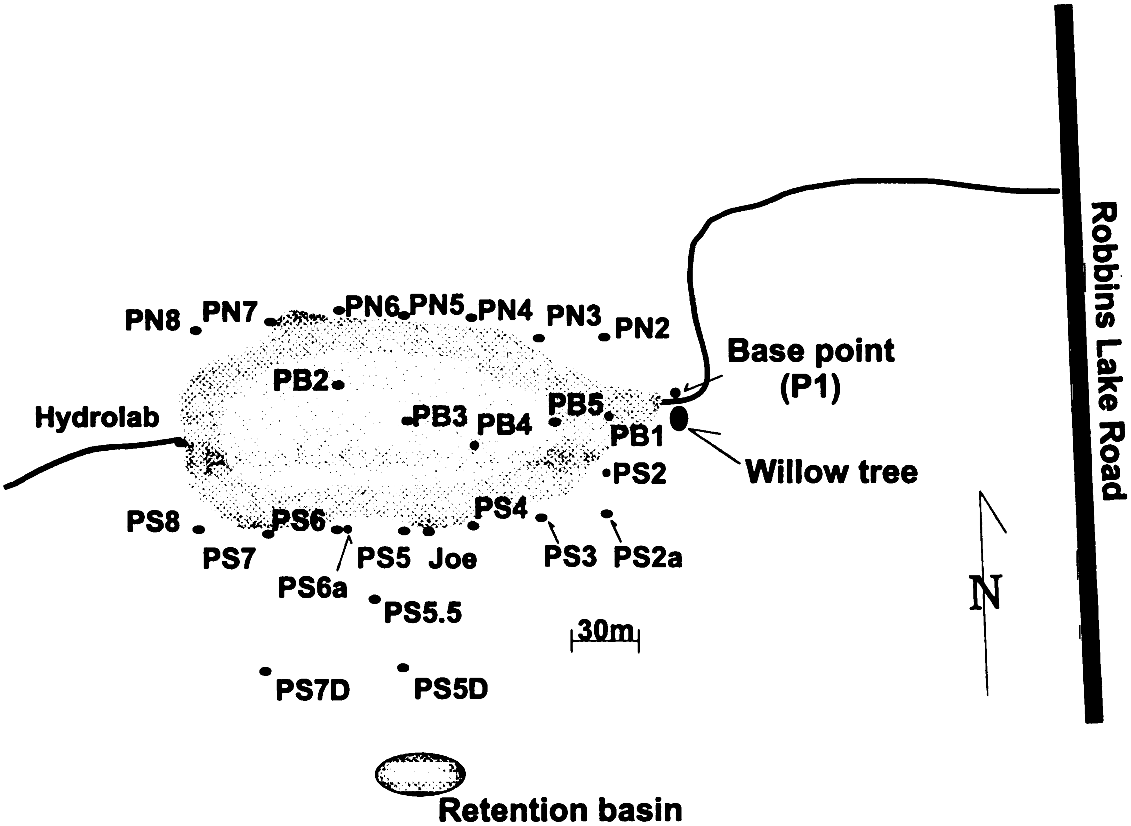

Figure 7: Locations of piezometers.

surface, which reduced the stability of the sides of the bore hole. At this point I drove a 10cm (3 inch) diameter, PVC pipe (schedule 40) into the bore hole using a 8cm (2.25 inch) hemispherical cap as a drive point. This method usually allowed some additional surface penetration, up to one meter (3 ft) in some cases. Using the capped PVC pipe as a sleeve, I next inserted a 3m (10 ft) length of 8cm (2.25 in) schedule 30 PVC. This smaller pipe had been perforated over the bottom 50cm (18 in) with eighty to one hundred 4mm (.25 in) holes. The perforated area was then covered with a nylon mesh to provide a filtering medium. A firm tap on top of the inner, smaller diameter PVC sufficed to dislodge the cap from the sleeve. The sleeve was then removed, leaving the piezometer in place. This method had the extra benefit of allowing the bore to collapse back onto the piezometer, rather than potentially compacting or "smearing" the material adjacent to the piezometer. Some mixing of water along the casing of the piezometer probably occurred in some instances, but it is fairly unlikely that mixing would have substantially changed the character of any of the samples.

One additional point of interest to this study was the large retention basin, upslope of the site on the south side. Because this basin could potentially be contributing N to the groundwater system, several piezometers were located upslope from the wetland in the anticipated path of flow. The bores were excavated using a bucket auger, with samples taken every 30cm (1 ft) to a depth of 150cm (5 ft), in a manner much like the other piezometers. However, because the saturated zone was in deeper than of 3m (the length of my outer PVC pipe) 12 inch PVC drive points were used as screens, with #10 slotted screening.

Within the wetland, two permanent piezometer nests were placed in the vegetative mat, one nest on the third ‘rung’ and one on the sixth ‘rung’ of the ladder system. Every attempt was made to place these nests both on the ‘rung’ and along the centerline of the wetland, but access and stability were serious concerns. These two nests consisted of one 2m (6.5 ft) length of 7 cm (2 inch) PVC and one 1m (3 ft) length, both perforated with approximately 50 4mm circular holes over the bottom 15cm (6 in). All piezometers used nylon mesh to help filter water entering the bore. The 2m (6.5 ft) length was forced into the wetland until refusal, and the 1m length was then fastened to the longer length with duct tape in such a way that the perforated portion, and only the perforated portion, was submerged. All piezometers mentioned were sampled eight times from September 30, 1996 to December 20, 1996, though many of the initial samples were used only for testing of the laboratory methods. One additional sampling was performed on May 22, 1997.

For the final two rounds of testing in 1996, a portable piezometer was constructed using a short length of perforated 250ml sample bottle covered in nylon mesh and attached to a pointed wooden stake. A 1m length of Teflon tubing was positioned inside the bottle and taped to the stake. At each sampling site this apparatus was inserted to the specified depth, using the point of the stake to push the vegetation and muck aside, and a sample extracted, starting at the surface and proceeding downward. At each depth, at least three bore volumes (approximately 1L) of water were extracted and discarded before the actual sample was collected.

Collection of samples was performed using a Nalgene brand hand-actuated vacuum pump and a two-holed stopper, in addition to rigid 250ml polycarbonate sample bottle. The pump was used to create a suction within the sample bottle, which then drew the water up the tube. Because the apparatus was reused, the bore was emptied entirely and allowed to refill prior to sample collection. After the bore refilled, one sample volume (250ml) was withdrawn to rinse with fresh sample water, then the actual sample was collected. In this way two objectives were achieved; 1) the sampling apparatus was thoroughly rinsed with water similar to the sample water, and 2) the water that had been exposed to the atmosphere in the piezometer was replaced with fresh water. Following collection, all water samples were stored in ice and processed within 24 hours of collection.

Rudimentary water chemistry data (temperature, pH, specific conductance, and dissolved oxygen content) were also collected using a Hydrolab Datasonde 3 (Hydrolab Corp., 12921 Burnet Rd., Austin, TX 78727). Measurements were made at each of the wetland sample sites and at each depth where water samples were collected during the final round of sampling. Additionally, the Datasonde was mounted at the outlet of the wetland from Oct. 13 - Oct. 16 1996, recording all of the above parameters every 30 minutes over this 72 hour period.

Water table elevations were recorded in the spring of 1997. Measurements were made relative to the top of the casing using an battery powered probe incremented in hundredths of feet. Casing elevations were measured in the spring of 1997 using a transit and stadia rod, relative to the top of the culvert protruding from the west side of Robbins Lake Road. Elevation of the culvert was estimated to be 880 ft (268 m) AMSL, based on the Jones, Michigan, USGS 7.5 minute topographic quadrangle.

SOIL SAMPLING

To achieve the objective of a three dimensional survey of mineral nitrogen reserves in the soil, a sampling scheme was devised to obtain multiple sample points at both different locations and depths across the site. Sample sites were laid out as extensions of the rungs of the ladder, and spaced at 30m (100 ft) intervals up-slope from the piezometers. In defining each soil sampling location, I used the appropriate piezometer as a starting point, a Brunton pocket transit for azimuth control, and a 30m hip-chain to define distance. I then proceeded to walk a vector due north or south of the respective piezometers. The piezometers were used as the base reference for measuring rather than the ends of each ladder rung so that the sites could be more easily identified for potential resampling later (Figure 8).

Site spacing was chosen for two reasons. First, the spacing seemed appropriate to the scale of study. The objective was to obtain a survey of nitrogen properties in the soil, not to intensive map N distributions. Second, as a practical consideration, weather and time constraints made the field component of even this sampling density difficult to complete before the onset of winter; a more dense sampling grid could not have effectively characterized as large an area.

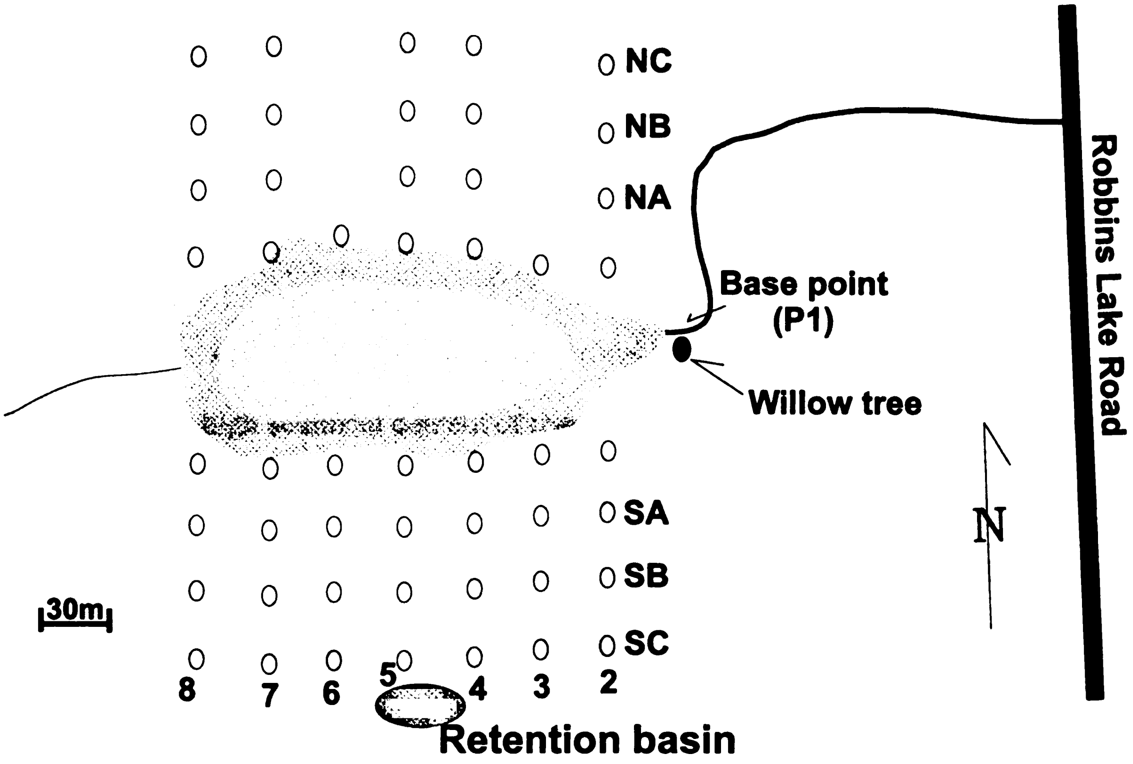

Figure 8: Locations of soil sampling sites.

At each sampling site, as many as five samples were collected. Soil samples were collected every 30cm (1 ft), starting at 30cm (1 ft), to a depth of 150cm (5 ft). All soil sampling was performed using a 10cm (3 inch) bucket auger with an open face to more effectively penetrate occasional gravel. At several sites, I encountered saturation before 150cm (5 ft). In these instances, deeper samples were not collected. In all, 263 soil samples were collected, including those taken during the installation of piezometers.

Following collection, all samples were stored in ice for the return from the field, then immediately frozen at field moisture in a -20°C freezer. Soils were stored frozen until I could perform NO_3^- and NH_4^+ extractions. Holding times ranged between 7 and 25 days, depending on how quickly the samples could be processed.

Lab Methods

WATER

Because of the high sediment content of many of the samples, extraction of mineral N was necessary to insure that N had not sorbed to the sediment. After a thorough shaking to obtain a uniform distribution of sediment within the sample bottle, a 50ml subsample was decanted off and added to 50ml of 2 M KCl in a 125ml Qorpak rectangular shaker bottle. This combination yielded a final supernatant with a KCl concentration of 1M. Salt concentrations higher that 1M frequently can cause mechanical difficulty in the injecting mechanism of the colorimetric ion analyzer (Ellis, personal communication, 1996). The samples were shaken on a reciprocating shaker at approximately 200 cycles per minute for 90 minutes.

After shaking, the solution and sediment were poured into 100ml centrifuge tubes and centrifuged for 5 minutes at 3800 rpm. In a few instances this period was insufficient to separate the water from the sediment, particularly in samples rich in organic material. In such cases, the sample was centrifuged a second time for the same period at the same speed. All samples yielded a clear supernatant after a second interval in the centrifuge.

The clear supernatant was decanted off, removing as much liquid as possible without contamination by either sediment or floating organic matter. The final supernatant solution was then placed into a 25ml scintillation vial, and stored at -20°C until processed on a Lachat QuikChem (Lachat Instruments, Inc., 6645 W. Mill Rd. Milwaukee, WI 53218) ion auto-analyzer. Calibration range was from 2ppm to 10ppm NO_3^- and NH_4^+ in solution. The apparatus uses cadmium reduction to convert nitrate to nitrite, then employed the colorimetric technique described in Keeney (1967).

SOILS

A variety of reagents have been used to extract mineral N from soils, though the most commonly used is KCl (Maynard and Kalra, 1993). Concentrations of KCl have also varied, ranging from 0.1M (Houba et. al. 1988) to 2.0M (Keeney and Nelson, 1982). I decided to use 1M KCl as a reagent for several reasons. First, some concern was expressed that high salt concentrations could adversely impact the Lachat (Ellis, personal communication, 1996). This concern could have been avoided by diluting the final supernatant, but that would have introduced an additional level of uncertainty into the N calculations. Second, the extraction process works by mass balance. In essence, the proportions of N to KCl in solution gradually come into balance with the proportions of N to KCl on the soil particles, as K^+ replaces NH_4^+ on the soil surface. Thus, while a higher concentration of KCl may yield a slightly more definitive estimate of mineral N, the difference is likely to be small. Indeed, Bremner (1965) found no difference in the quantity of N extracted by 1N KCl as opposed to 2N KCl.

The process for extracting N from soil samples is very similar to that used for extracting N from the water samples, and is described in both Maynard and Kalra (1982) and Bremner (1965). First, a 5g sample of the field moist soil was weighed and placed into a 125ml Qorpack rectangular shaker bottle. Simultaneously, I measured a second 5g sample and placed it into a tared 50ml beaker. This second sample was dried for 48 hours at 105°C and used to determine its gravimetric soil moisture content. The former sample was shaken for 90 minutes with 50ml of 1M KCl solution on a reciprocating shaker at approximately 200 cycles per minute. The sample was then transferred to a 100ml centrifuge tube, and centrifuged at 3800 rpm for 5 minutes, to separate the sediment from the supernatant. In some cases, an additional interval in the centrifuge was required to fully drive the solid material to the bottom of the tube.

Once the sediment had been separated from the solution, a 50ml aliquot was pipetted off and stored frozen in two 25ml scintillation vials at -20°C. Analysis was then performed using a Lachat QuikChem ion auto-analyzer. The calibration range for soil samples was from 1ppm to 5ppm NO_3^- and NH_4^+ in solution.

Additional procedures

Some concern had been expressed by several researchers at the Institute for Water Research at Michigan State University as to the accuracy of nitrate/nitrite test strips (Aquachek Environmental Test Systems, Inc. P.O. Box 4659 Elkhart, IN 46514) for field estimates of nitrate and nitrite concentration in water. To address this issue, during the final run of water samples, half of all the water samples were measured using test strips, and the result recorded, prior to processing of the samples using the methods described above.

Chapter 4

RESULTS

The data collected in this study are shaped, to a much larger extent than expected, by the local geologic surroundings. In fact, as will be seen shortly, the stratigraphy within the soil and glacial deposits immediately surrounding the wetland is the controlling factor in the rest of the hydrological, geochemical, and microbiological processes examined at the site.

Hydrologic and Stratigraphic Properties of the Site

Coring to install piezometers and to obtain soil samples exposed a layer of gleyed, silty clay underlying the wetland and much of the surrounding area, extending back to a distance of between 5 and 20 meters from the apparent border of the wetland. The gleyed material is probably lacustrine or glaciolacustrine in origin, and is at least 50cm thick at all points probed, and in some places over 100cm in thickness. The varying thickness of the overlying muck and vegetation limited the depth of probing, although nowhere within the wetland was the silty clay layer penetrated. Based on data from the edges of the wetland, where the gleyed layer *was* penetrated, the silty clay layer is probably thickest in the center of the wetland, gradually thinning until it ceases to exist at an elevation approximately 2 meters above the average current level of the muck in the wetland.

Geophysical exploration of the wetland and immediate surroundings was conducted with a 3cm (1 in) diameter screw auger at 15 points within the wetland. This investigation revealed a second lithologic discontinuity along the southern margin of the wetland, between transects 3 and 7, wherein mineral material was superimposed on top of organic muck (Figure 9). This colluvial material was sandy loam in texture, generally similar to what is found at the surface upslope from the wetland. This mineral layer is generally no more than 15cm (6 in) in thickness, strongly suggestive of prior (upslope) erosional activity at the site. Not surprisingly, neither the silty clay layer nor the superimposed mineral soils are part of the profile description for the Adrian muck.

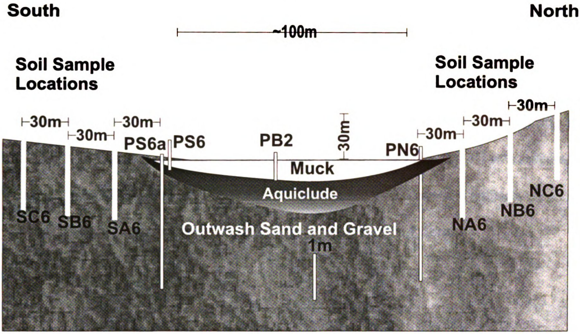

Figure 9: Cross-section of the wetland at transect 6.

While installing the piezometers, it became evident that the silty clay serves as an aquiclude that separates an aquifer system beneath the wetland (in the sand and gravel material) from the muck and more rapidly flowing waters of the wetland proper. While coring in the fall of 1996 in unsaturated soils beyond the edge of the muck, but still above the basin formed by the silty clay layer, I observed that once the clay layer was punctured, previously dry soil borings filled with water. This observation suggested that two local aquifers exist at the site, one that is confined by the silty clay layer, deeper in the glacial outwash deposits and under some artesian pressure, and one that is shallower, perched in the primarily organic materials above the silty clay layer.

This conclusion was verified the following spring by interpreting measurements of hydraulic head differences (see Table 1). Typically, if both the wetland and the sand and gravel aquifer were one connected system, water table elevations would be similar, if not identical, in piezometers above and below the silty clay layer. However, substantial differences were found between piezometers installed above the silty clay layer and those installed either through or beyond the stratum. These measurements were made during a particularly dry spring, so in fact the relationship observed the previous fall was reversed. Whereas in the fall the deeper glacial aquifer appeared to be under some artesian pressure, confined by the aquiclude, in the spring the level of the deeper

Table.1: Water table elevations observed in piezometers, May 22, 1997. Shaded cells indicate piezometers interpreted to be sampling below the aquiclude. See Figure 7 for locations.

Site	Top of Casing	Land surface correction	Land surface elevation	Water Elevation
HYDROLAB	866.65	0.00	866.65	866.65
PS8	872.28	3.52	868.76	867.41
PS7	872.56	3.60	868.96	867.52
PS6	874.10	5.64	868.46	867.48
PS4	873.85	2.86	870.99	868.77
PS3	873.44	3.14	870.30	869.13
PS2A	874.41	3.72	870.69	869.02
PS2	870.80	0.74	870.06	869.15
PN2	879.20	3.20	876.00	869.80
P1	871.60	1.40	870.20	870.10
P1STREAM SURF	869.54	0.00	869.54	869.54
PS6A	870.86	2.34	868.52	864.68
PS5D	885.38	3.81	881.57	867.00
PS5.5	878.70	0.52	878.18	866.20
PS5	872.89	1.44	871.45	864.70
JOE	872.69	1.22	871.47	865.10
PN8	876.00	1.58	874.42	865.23
PN7	873.70	2.40	871.30	865.14
PN6	870.40	1.62	878.78	864.82
PN5	872.90	2.28	870.62	865.19
PN4	873.90	2.46	871.44	865.31
PN3	875.94	4.18	871.76	865.32

groundwater aquifer[1] had dropped, such that the water in the wetland was now actually perched above the aquiclude (Figure 10).

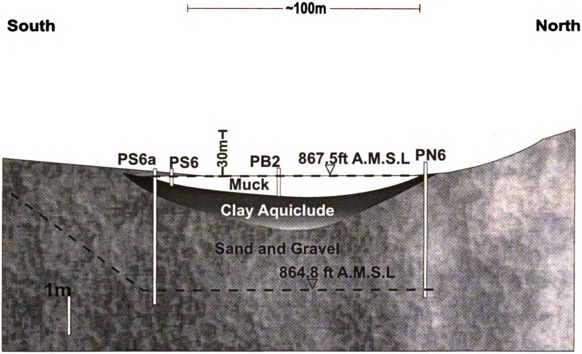

Figure 10: Cross-section of wetland showing water levels.

At various points over the past century or so, overland flow and erosion were clearly present at the site, evidenced both in the mineral material found overlying the wetland muck, and in historic aerial photography of the site (see Appendix B). Observations made recently at the site during rain, snow, and snow melt events indicate that there is currently very little potential for overland flow of water into the wetland. The soils

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[1] Hereafter 'ground water' refers to the waters within the sand and gravel aquifer only.

upslope at the site are coarse textured, and the land owner has recently implemented more conservative soil management practices, such as riparian buffers and no-till farming. Thus, in all but the most severe precipitation events, overland flow cannot be a substantial contributor of nitrogen to the wetland.

Differences in the oxidation-reduction (redox) conditions between the aquifers were also apparent when installing the piezometers. The silty clay layer was frequently gleyed (Munsell color 2.5Y 6/2), implying a reducing environment. Conversely, soils below this layer exhibited lighter reddish-yellow hues (Munsell color 10YR 3/6), indicative of oxidized iron species, and hence aerobic conditions. This difference will become significant in the discussion of nitrogen oxidation states later.

In conclusion, the bulk of this physical and chemical evidence indicates that two separate aquifer systems, with locally distinct contributing areas, exist at the site. One aquifer system occurs in the sand and gravel below the site and is probably the regional glacial aquifer (Kehew et al. 1996; Ervin et al. 1995). This aquifer system is completely separated from the wetland, though the small stream flowing into the wetland may be fed in part or in whole by this deeper aquifer. Groundwater may contribute to flow within the wetland, but only through additions to the tributary stream. The other aquifer occurs above the silty clay layer, is of very limited extent, and mixes freely both with the muck and the inflow from the stream (Figure 11). Finally, observations indicate that there is no overland flow into the wetland, save the small stream flowing in from the east. While the stream may technically contain water originating from the sand and gravel aquifer, the stream will be discussed in conjunction with the wetland system, because inputs from the stream were isolated by a piezometer at the head of the wetland. Because of the evidence demonstrating that two separate hydrologic systems exist at the site, each system will be discussed individually.

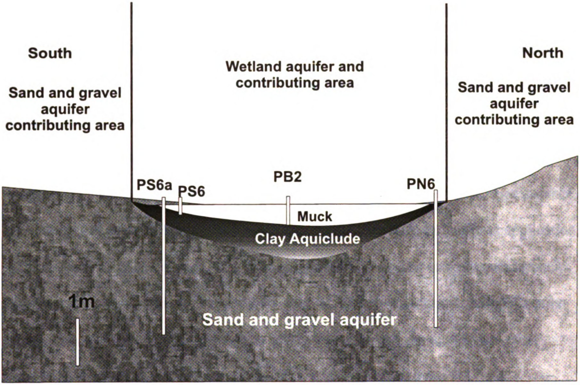

Figure 11: Cross section of wetland showing contributing areas.

The groundwater system and upland soils

NITROGEN CHARACTERISTICS OF THE UPLAND MINERAL SOILS

Soil samples analyzed for residual nitrogen were collected between December 1, 1996 and January 15, 1997. Mineral N was reported as a concentration of either NH_4^+ or NO_3^-

in water. To convert these concentrations into more typical weight/area agricultural units, it was necessary to extrapolate each sample to either an acre or a hectare in area, and one foot (30 cm) thickness. For convenience, the bulk density of the soil was assumed to be 1.5 g/cm^3 (NRCS reports a range from 1.35 to 1.6 for the upland soil series at the study area). Seventy-one percent of the samples measured contained less than 17.8 kg/ha (20 lbs/acre) total residual N (see appendix C). Given that typical N application rates range from 135 to 178 kg/ha (150 to 200 lbs/acre), this represents a total over-application residual of approximately 10%. From an agronomic standpoint this over-application is acceptable, possibly even desirable, because it means that the crop is not nutrient-limited.

Judged from a water quality perspective, however, more subtle issues arise. For instance, expressing N in terms of weight/area is sensible within the context of nutrient application, but a measure on a weight/weight basis is more useful for assessments of contamination. Similarly, a problem exists in the way NO_3^- data are typically analyzed. Nitrate is often presented as a weight of NO_3^- per weight of dry soil. This representation, however, ignores the facts that 1) the NO_3^- ion is highly soluble throughout normal field temperatures and 2) the NO_3^- anion does not sorb to most soil particles or associate with common solution cations. These two points indicate that if NO_3^- is present in the soil, and the soil is moist, then the NO_3^- is probably in the aqueous phase, and thus essentially independent of the soil particles, *i.e.*, readily leached. Consequently, the appropriate way to express NO_3^- loadings with an eye to water quality assessments is as a weight/volume of pore water in the soil. However, the question arises of which pore water measurement to use; potential pore water after drainage (field capacity) or actual pore water (some value less than field capacity).

To address this question we need to recall Hillel's (1982) description of the properties of water movement in the soil. Water only drains from a soil pore when the field capacity is exceeded. Thus, any time the water content of the soil is below field capacity, the pore water is attenuated within the matrix, and is slowly accumulating NO_3^- as any NH_4^+ present is nitrified. However, for ground-water recharge to occur, field capacity must be exceeded throughout the thickness of the soil profile, from the surface to the water table. Only at this point, when ground-water recharge is occurring, does NO_3^- contamination become a drinking water problem.

When infiltration does occur, this NO_3^--enriched water will be displaced by comparatively cleaner water infiltrating from above. Thus, while the *in situ* water will likely be diluted by diffusion processes in transit (Hillel, 1982), the net effect will be to compact the NO_3^- enriched water from throughout the upper portions of the profile into a zone above the wetting front but below the newly infiltrated "cleaner" water from the surface. Thus, it would not be surprising to find higher concentrations of NO_3^- in the soil water deeper in the vadose zone. Therefore, the reasonable solvent volume to consider is the actual pore water at the time of sampling; this *in situ* water, essentially unchanged, will be the first water to reach the aquifer during a recharge event. All NO_3^- values will be reported as parts per million (ppm) of NO_3^- in the actual pore water.

Figures 12 - 16 and 17 - 21 show the concentrations of NO_3^- and NH_4^+, respectively, at five sampling depths. The most evident pattern is the elevated levels of both forms of nitrogen in the southeastern section of the study area. This horizontal distribution pattern is the result of corn being grown in that southeastern portion, whereas the rest of the study area is pasture. Corn crops receive, and can utilize, much more N than the adjoining pasture. However, it appears as though the corn is not fully utilizing the N available.

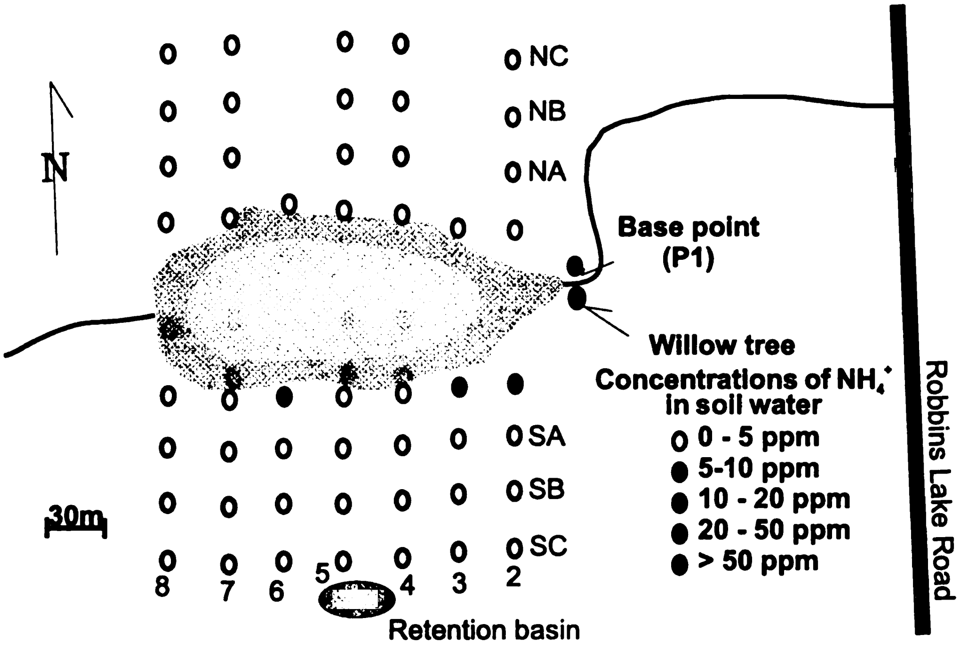

Figure 12: Ammonium concentrations at 30 cm (1 ft).

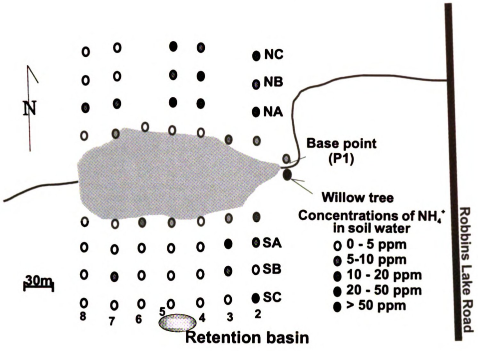

Figure 13: Ammonium concentrations at 60 cm (2 ft).

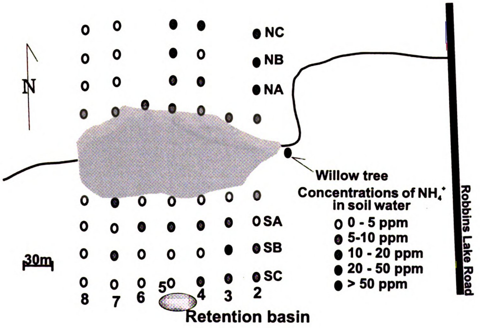

Figure 14: Ammonium concentrations at 90 cm (3 ft).

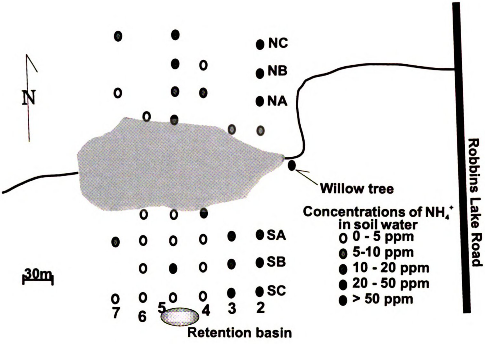

Figure 15: Ammonium concentrations at 120 cm (4 ft).

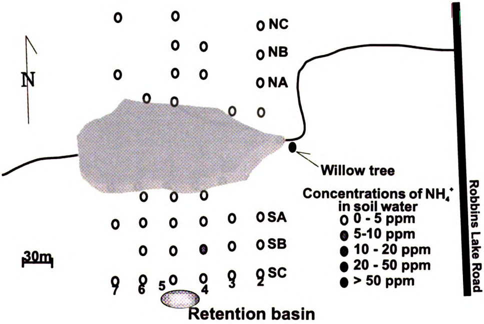

Figure 16: Ammonium concentrations at 150 cm (5 ft).

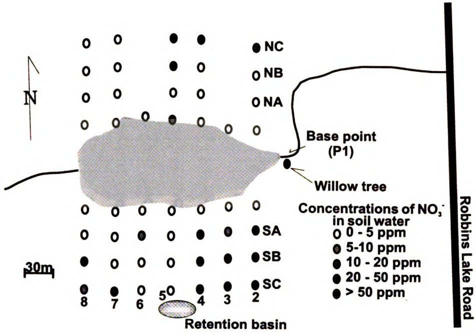

Figure 17: Nitrate concentrations at 30 cm (1 ft).

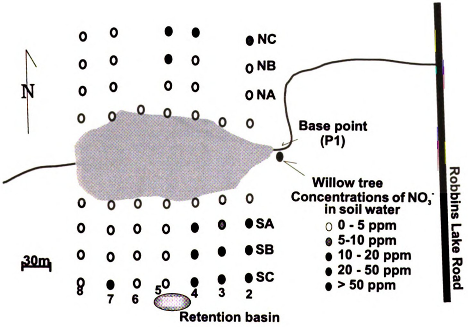

Figure 18: Nitrate concentrations at 60 cm (2 ft).

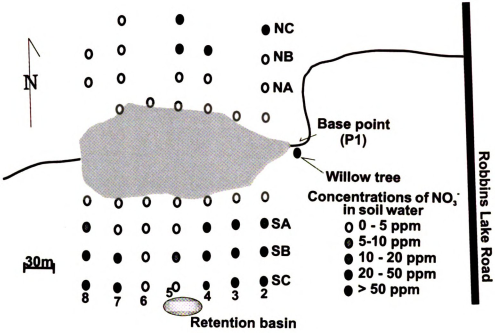

Figure 19: Nitrate concentrations at 90 cm (3 ft).

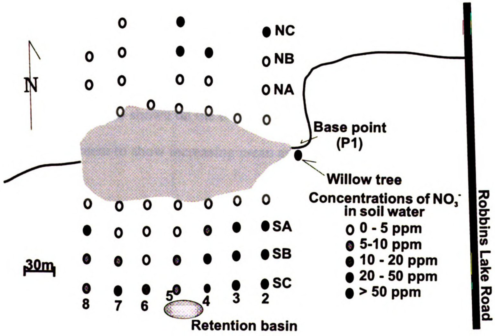

Figure 20: Nitrate concentrations at 120 cm (4 ft).

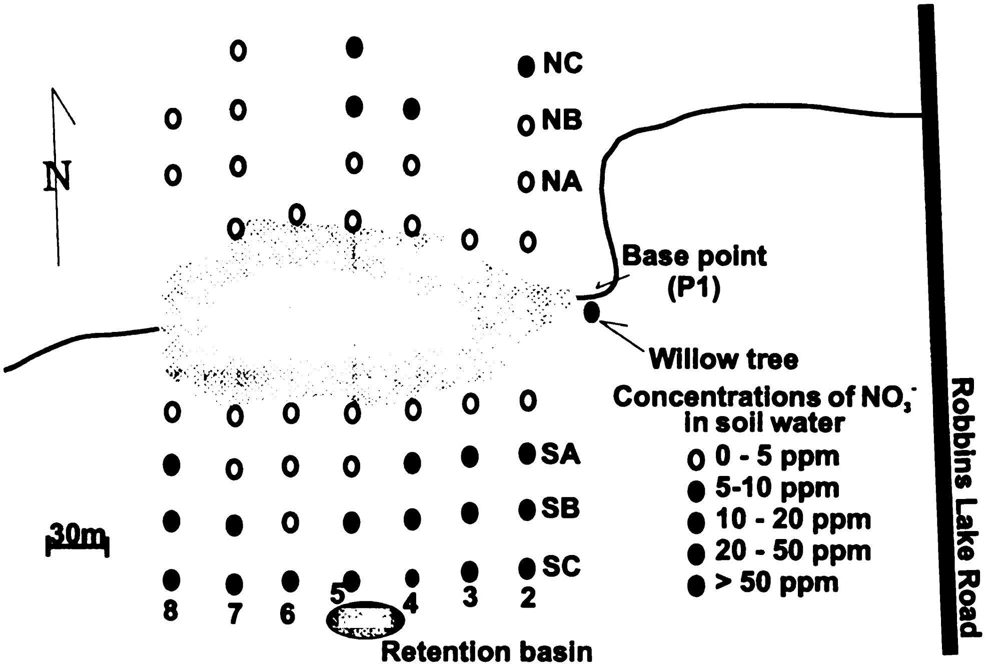

Figure 21: Nitrate concentrations at 150 cm (5 ft).

By comparing the concentrations of NO_3^- in Figures 17 - 21, a feel for the vertical distribution of NO_3^- within the soil column can be gleaned. The vertical distribution of NO_3^- generally shows an increase in dissolved concentration with depth. This apparent relationship is also shown on the boxplots of concentrations vs. depth (figures 22 and 23), which also seem to show increasing mean and maximum concentrations with increasing depth.

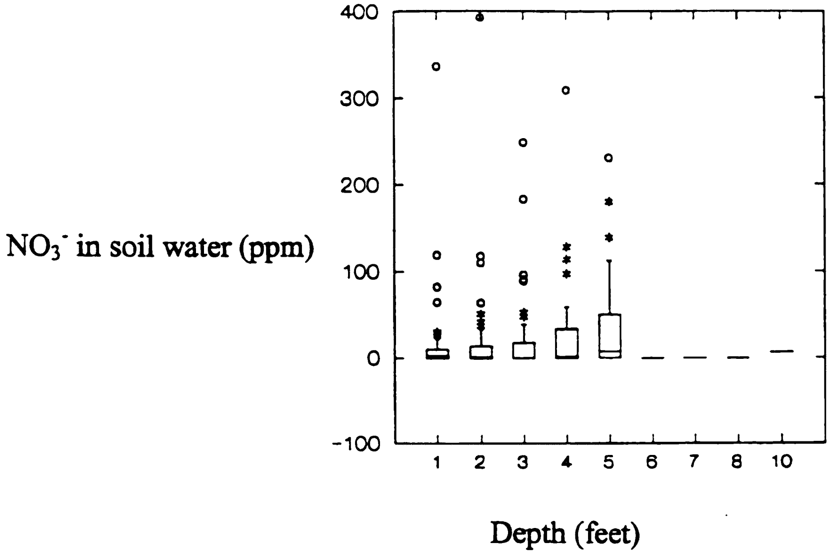

Figure 22: Boxplot of NO_3^- data from the Robbins Lake Road site. Notice the increasing mean and 25th percentile values with depth.

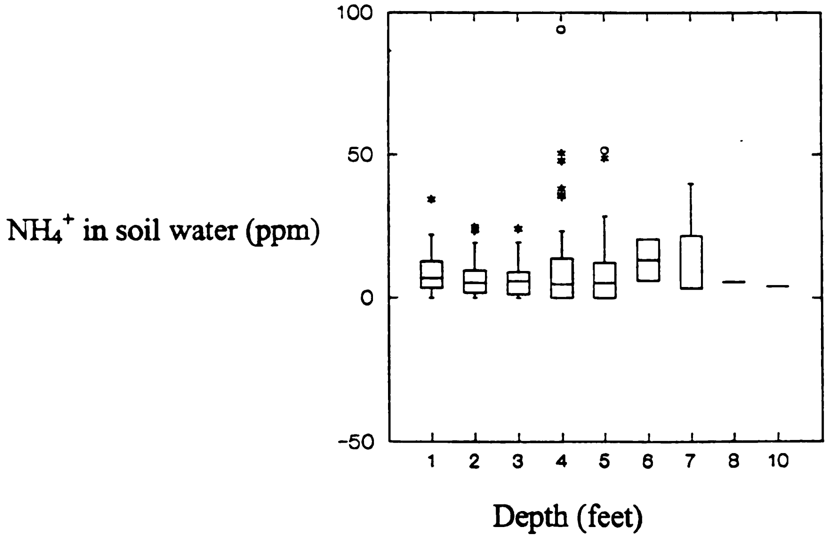

Figure 23: Boxplot of NH_4^+ data from the Robbins Lake Road site. A general increase in concentration still appears to occur with depth.

Site SC2 emphasizes the importance of managing N application rates based on specific crop needs. This site is located in a small swale planted in grass amidst the area planted in corn. The swale is perhaps only 30 m^2, and receives the same N application as the corn. Soils sampled at site SC2 had, by a substantial margin, the highest NO_3^- values found anywhere at the site (see Figure 24 and Appendix C). The uptake of N by grass is substantially less than that of corn, probably resulting in the very high residual values found. This small area almost certainly contributes NO_3^- to the groundwater.

The overall conclusion from the analysis of the upland soils is that there is an N surplus, particularly in the southeast portion of the study area, the section planted in corn. The presence of surplus residual N opens the possibility for NO_3^- leaching, and potential groundwater contamination. The samples from the area planted in corn (and fertilized for corn) had substantially higher NO_3^- values than the areas that were in pasture, with the exception of the small grassy area embedded within the corn, where NO_3^- values were exceptionally high. This excess NO_3^- almost certainly results in excessive NO_3^- loadings

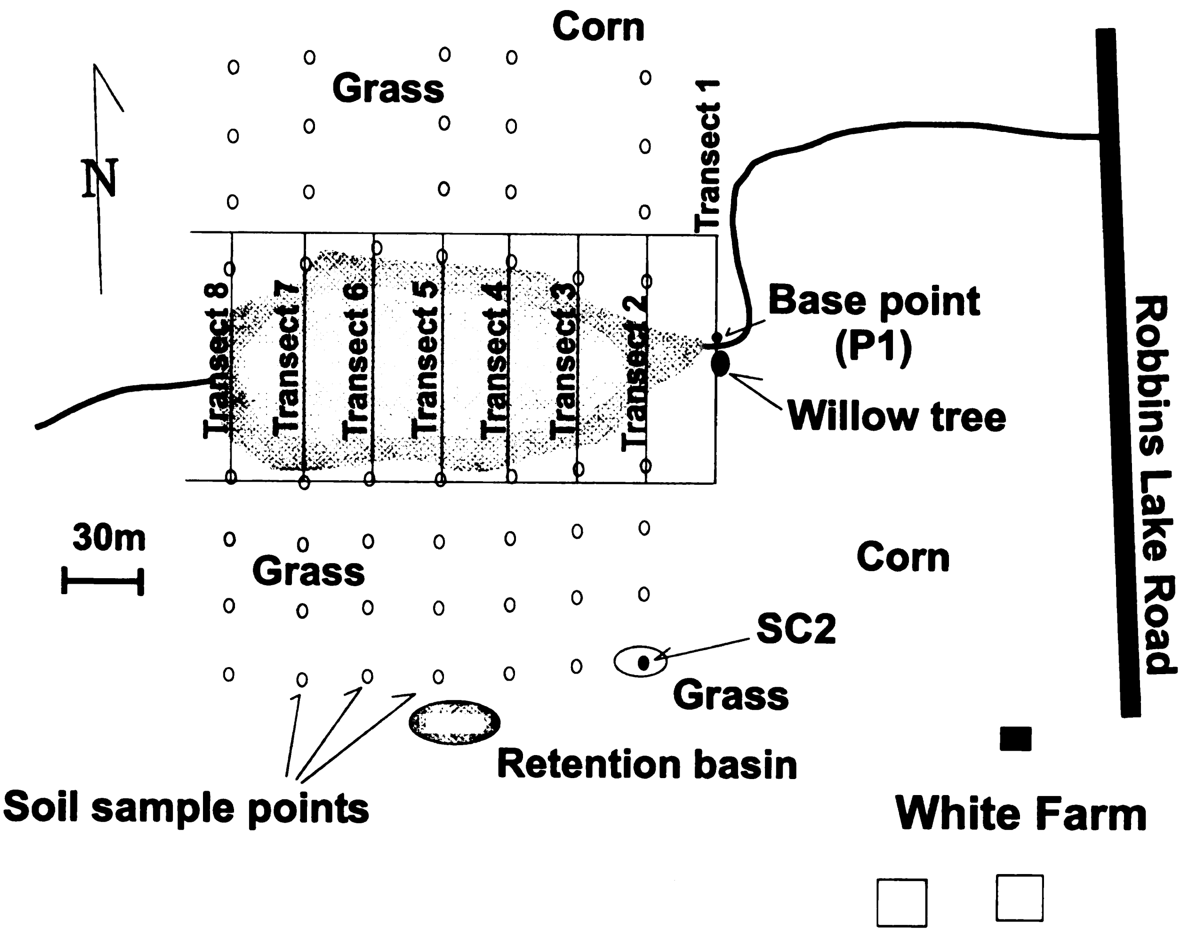

Figure 24: Location of soil sample site SC2.

to the regional (outwash) aquifer but, because of the aquiclude separating the groundwater from the wetland, the excess N of the upland soils, and possible contamination of the underlying groundwater, has virtually no impact on the water quality within the wetland.

NITROGEN PROPERTIES OF GROUNDWATER

Sub-surface water samples were collected from piezometers on three separate occasions (12/7/96, 12/13/96, and 5/22/97), twice in late fall and once in the spring. Sampling sites are shown in Figure 25. These samples were then analyzed for inorganic forms of N. The results of the three replicates of groundwater sampling are shown in table 4.2. Of the 12 sites sampled, five had NO_3^- levels in excess of the EPA Maximum Contaminant Level (MCL) of 10 ppm during the two fall samplings. All the sample sites in excess of the MCL were on the south side of the wetland, and likely down gradient from the retention basin used to capture runoff from the upslope fields beyond the study site. Notice that these sites, particularly the upslope ones, are not down gradient from the swale surrounding SC2. While not conclusive, it seems likely that these elevated levels are the result of a NO_3^- plume originating in the sediments of the retention basin (figure 4.9). The possibility does exist, however, that the fields upslope, and beyond the study area, are contributing NO_3^-. Elsewhere, the sampled groundwater contained NO_3^- in concentrations that are comparable to the rest of the Donnell Lake watershed (Ervin, personal communication, 1997). Levels ranged from 0.5 ppm to 5 ppm (Table 2). A small NO_3^- plume could also be inferred to be on the north side of the wetland, with peak

Table 2: Results of groundwater sampling. All values are in ppm, shading indicates piezometers sampling below the aquiclude.

	Collected 12/7/96		Collected 12/13/96		Collected 5/22/97	
Location	NO_3	NH_4	NO_3	NH_4	NO3	NH4
PS8	0.1	0.16	0.2	0	0.77	0.02
PS7D	12.72	0.12	12.82	0	6.85	0.26
PS7	0	1.76	0	1.5	0	0.54
PS6A	11.94	0.14	10.68	0.24	0.29	0
PS6	0	6.26	0	4.36	0	9.75
PS5D	10.18	0	9.82	0.22	7.91	0
PS5.5	16.62	0.06	15.82	0.16	2.33	0.22
PS5	0.38	0.22	0.12	0.32	1.88	0.19
Joes	11.06	0.14	8.52	0.24	0.92	0.14
PS4	0	1.98	0	0	0	0.84
PS3	0	1.38	0	1.4	0.14	0.06
PS2A	0.16	0.1	0.14	0.12	0	0.1
PS2	0.08	0.04	0.06	0.18	0	0.13
P1	1	0.3	1.24	0.2	0	0.05
PN2	0.28	0	0.32	0.24	0.14	0.04
PN3	1.32	0.1	1.48	0.32	0	0
PN4	0.28	0.1	0.28	0	2.71	0.03
PN5	1.62	0.12	3.56	0	0.16	0.03
PN6	3.7	0.06	5.4	0.24	0.14	0.02
PN7	4.04	0.22	4.38	0.12	0.13	0
PN8	0.58	0	0.84	0.22	0.2	0.05

levels of approximately 5ppm NO_3^-, between transects 5 and 7. Presumably this plume is moving south, and probably originates in the corn field to the north (Figure 25).

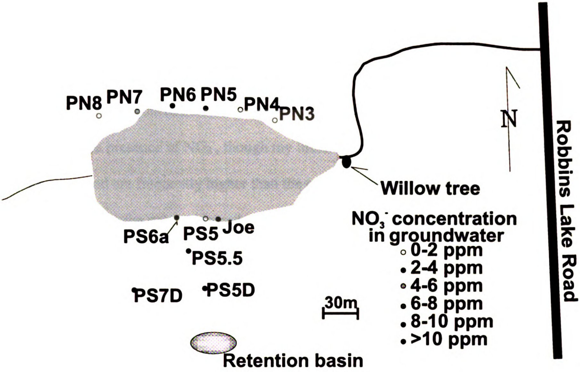

Figure 25: Locations of groundwater piezometers and nitrate concentrations.

<u>The wetland system (above the aquiclude)</u>

Previous investigations by the MSU Institute for Water Research (D. Lusch and J. Ervin, personal communication, 1996) had indicated a rapid increase in NO_3^- concentrations in the stream and possibly in the muck, beginning approximately halfway up the long axis of the wetland. In many ways, their finding was the primary impetus for this specific project. Consequently, water samples were obtained from piezometers along the long axis of the wetland at 30m intervals to reconfirm their findings. The results generally concur with the observations of the Institute, though some discrepancy was revealed in the concentrations, probably as a result of a somewhat more precise method of measurement. The investigators from the Institute used a test strip field method (Ervin, personal communication, 1996), as opposed to the colorimetric laboratory method (see Chapter 3) used here. Half of the samples obtained in May 1997 were analyzed by both methods, and while the test strips were obviously less precise, both methods reported similar approximate concentrations (table 3). The test strip method is appropriate for establishing the presence of NO_3^-, though my limited data indicate that results from the test strip method are frequently higher than the colorimetric method, sometimes approaching twice the value obtained colorimetrically. However, in no case did the test strips indicate a false positive value.

Table 3: Comparative data values Colorimetric and test strip methods of analysis. Samples were collected 5/22/97.

	Colorimetric	Strip
Location	NO_3^-	NO_3^-
PS8	0.77	0
PS7	0	0
PS6A	0.29	8
PS6	0	0
PS5D	7.91	20
Joes	0.92	2
PS2A	0	0
PN2	0.14	0
PN8	0.2	0
PB4 15cm	2.02	2
PB1 0cm	0.77	2
PB3 15cm	2.13	4
Hydrolab 0cm	1.24	3
PB3 0cm	2.63	7
PB4 0cm	2.24	3
PB2 45cm	0	0
PB2 30cm	0	0

The results of the surface survey can be found in Tables 4-6, listed as samples taken at a depth of 0cm. Nitrate is present at the inflow of the wetland (site P1) at levels of 2-3 ppm, then levels increase to approximately 7-9 ppm near transect 4 (site PB4), only to decline to 3-5 ppm by transect 8 (site Hydrolab). The results from the different sampling dates do not agree perfectly, which is why these are reported only as ranges. Data from the spring sampling are not included because these values were substantially different. The causes of this change could vary from differences in microbial habitat with differing temperature to changes in plant uptake based on different portions of the growing season.

Table 4: Results of Dec. 7, 1996 sampling.

West East

Site	Hydrolab		PB2		PB3		PB4		PB5		PB1		P1	
Depth	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+
0 cm	3.54	0.06	7.04	0.12	7.38	0.14	9.14	0	2.5	0.16	4.1	0.12	2.18	0.04
15 cm	3.16	0.1	6.78	0.18	7.08	0	8.32	0	0.52	0.66				
30 cm			5.66	3.26	4.34	1.18	5.9	3.16			2.84	2.02		
45 cm			0	10.1										

Table 5: Results of December 13, 1996 sampling.

West East

Site	Hydrolab		PB2		PB3		PB4		PB5		PB1		P1	
Depth	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+
0 cm	5	0.68	7.58	0.24	6.46	0.24	7.58	0.18	5.36	0.14	4.22	0.34	2.92	0.18
15 cm	5.06	0.2	4.66	0	7.68	0.32	9.34	0.14	2.2	0.62				
30 cm			4.26	2.28	4.76	0.64	4.24	2.74			0	2.31		
45 cm			0	7.32										

Table 6: Results of May 22, 1997 sampling.

West East

Site	Hydrolab		PB2		PB3		PB4		PB5		PB1		P1	
Depth	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+
0 cm	1.24	0.04	2.67	0	2.63	0	2.24	0	1.65	0.02	1.46	0	0.77	0.02
15 cm	1.2	0.02	2.45	0	2.13	0.25	2.02	0.4						
30 cm			0	10.72	1.8	0.42	1.46	0.05			0.09	0		
45 cm			0	10.11										

In summary, the Institute's findings were reconfirmed, but these data are only one portion of the complex chemical situation within the wetland.

As a preliminary step, pools along the long axis of the wetland were profiled using a Hydrolab Datasonde 3 on October 19, 1996 (Hydrolab Corp, 12921 Burnet Rd, Austin, TX 78727). The Hydrolab measures temperature, specific conductance, dissolved oxygen (DO), and pH of water *in situ*. The results (Tables 7 - 10) provide some very significant implications for this study. Peculiarly, some of the parameters exhibit variation with depth and distance, while others exhibit virtually none. Two of the four parameters, pH and specific conductance, exhibited very little variation across the wetland. Temperature varied between 4.15 °C and 7.85 °C, though this was probably due to variable snow cover on the wetland at the time of sampling in December. The air temperature was about 2°C and a very bright sun was shining on the wetland, and absorbance probably

Table 7 : Temperature (°C) characteristics of the wetland.

Depth	Hydrolab	PB2	PB3	PB4	PB5	PB1	P1
0 cm	4.15	5.62	6.00	7.53	6.32	5.15	5.43
15 cm	4.16	5.60	6.02	7.50	6.76	5.45	
30 cm		5.60	6.05	7.60			
45 cm		5.60	6.07	7.85			

Note: Air Temperature at time of sampling ~ 5 °C. Previous night's low, -3°C.

Table 8: Specific Conductance (*u*s/cm) characteristics of the wetland.

Depth	Hydrolab	PB2	PB3	PB4	PB5	PB1	P1
0 cm	580	610	601	640	556	535	558
15 cm	578	613	597	631	558	534	
30 cm		611	589	614			
45 cm		605	580	607			

Table 9: pH characteristics of the wetland.

Depth	Hydrolab	PB2	PB3	PB4	PB5	PB1	P1
0 cm	8.04	8.04	8.20	8.02	8.05	8.19	8.11
15 cm	8.30	8.18	8.11	8.03	8.10	8.15	
30 cm		8.08	8.12	8.01			
45 cm		8.03	8.10	7.97			

Table 10: Dissolved Oxygen (mg/L) characteristics of the wetland.

Depth	Hydrolab	PB2	PB3	PB4	PB5	PB1	P1
0 cm	10.6	8.28	7.95	5.2	5.89	6.8	6.22
15 cm	9.75	7.05	0.25	3.8	0.25	5.15	
30 cm		0.45	0.4	0.52			
45 cm		0.05	0.05	0.06			

varied greatly between snow covered areas, areas with vegetation, and areas with open water.

The most significant chemical variation was the profound and continuous gradient in DO, which decreased with depth. Near the surface the conditions are clearly aerobic, with DO readings between 5.2 ppm and 10.6 ppm. Sub-surface waters, specifically those below about 30cm, are anaerobic, with readings varying between 0.5 ppm and 0.05 ppm. As a reference to how low those DO values are, fish cannot survive in water with DO lower than 5 ppm (Bolsenga and Herdendorf, 1993). It is important to note that the Hydrolab's DO probe was at the low end of its operating range, and the values obtained are better considered as approximations than as actual measurements.

The significance of these measurements is that they indicate something about the mixing of water (and consequently dissolved materials) present within the wetland. DO has been observed to change within a matter of minutes at other wetlands in the Donnell Lake watershed because of a moving vegetation mat (Lusch, personal communication, 1996). While there is no such moving mat in this wetland, the example speaks to the rapid variability of DO. The fact that water temperature is varying horizontally, as opposed to vertically, is rather peculiar, and indicative of mixing. In a lacustrine situation, it is common for the surface layer to become either much warmer or much cooler than the deeper water, depending on the temperature of the atmosphere (usually based on the season) relative to the lake (Drever, 1988; Wetzel, 1982). This difference in temperature can result in a thermocline that effectively prevents mixing of the waters. At the research site, however, temperatures vary across the wetland, giving every indication that there is very little vertical variation. Thus, I conclude that 1) there *is* mixing occurring in the wetland, and 2) there exists a clear break at a depth of 30cm between an aerobic zone (above) and an anaerobic zone (below). While these two findings may appear to conflict, the key is understanding the relevant time scale. Water mixing may take place over hours or perhaps even days, while the consumption of available oxygen can happen in a time frame of minutes to hours (Mitsch and Gosselink, 1993). Thus, water is slowly passing between these two zones, reacting rapidly in both aerobic and anaerobic environments within the wetland system.

This aerobic/anaerobic distinction of water within the wetland is very important in considerations of nitrogen transport and transformation, because nitrogen is very sensitive to changes in redox conditions (Drever, 1988; Lovley 1994). Lovley(1994), among others, has repeatedly identified NO_3^- as the first commonly available terminal electron acceptor to be utilized by microbial processes in anaerobic environments. Thus, once free oxygen is removed, NO_3^- is the next most appealing source of oxygen for microbial processes, resulting in what has been known for years as denitrification (see chapter 2). An important distinction should be reiterated here. While NH_4^+ can be oxidized into NO_2^- and NO_3^-, NO_3^- and NO_2^- are not reduced to NH_4^+, but are rather released in the gas phase as N_2O and N_2

The results of the NO_3^- and NH_4^+ analyses of water within the wetland muck are shown in Tables 4 - 6. NH_4^+ is routinely present, in concentrations as high as 10 ppm, in the deep water samples, and yet, is routinely absent in the shallower water samples. These occurrences correlate with the NH_4^+ observed in the piezometers (PS4, PS6 and PS7) at the edge of the wetland, sampling above the silty clay layer (Figure 26). These three piezometers are in the same area along the southern margin of the wetland where mineral soils were observed overlying organic muck. The piezometers are sampling water that saturates the muck.

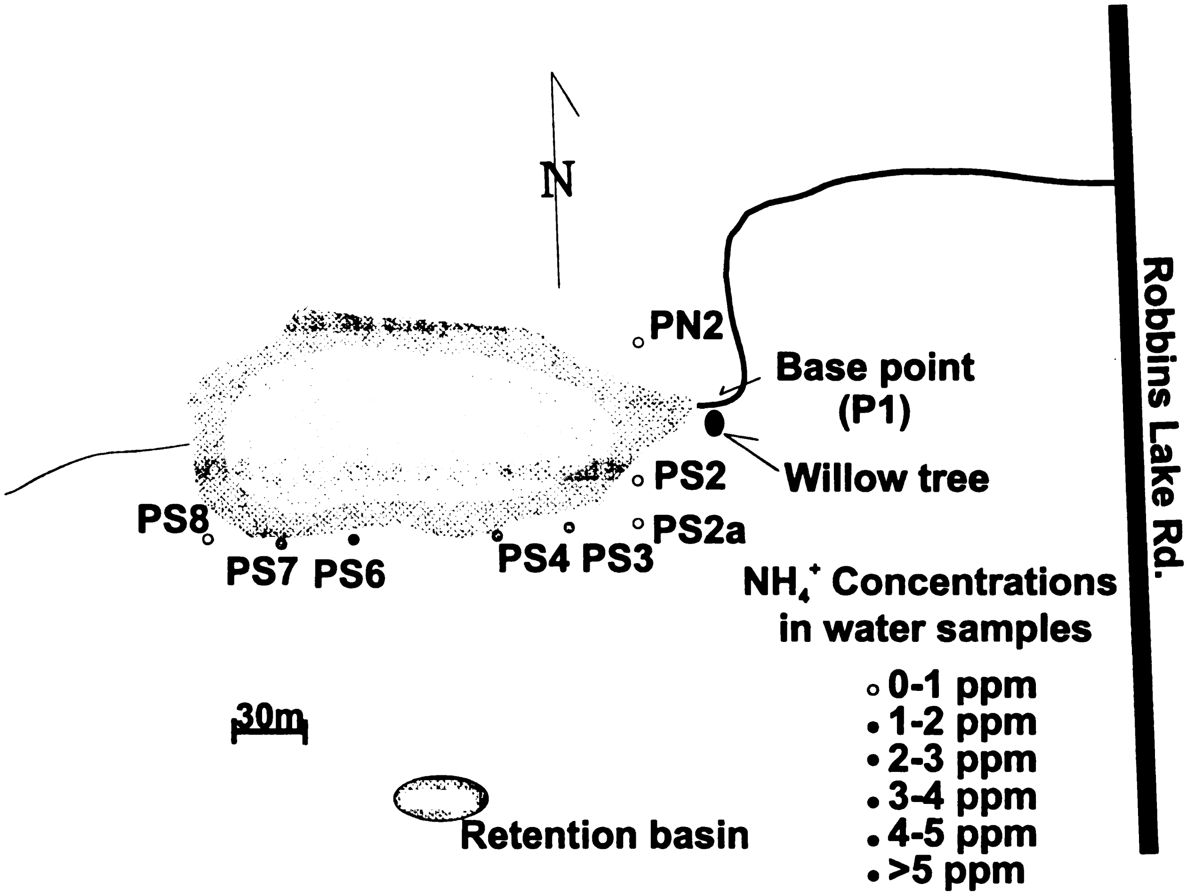

Figure 26: Locations of single depth piezometers sampling the wetland system and ammonium concetrations.

There is a consistent pattern of NH_4^+ occurring in solution in the deeper parts of the wetland. These NH_4^+ concentrations are approximately the same as NO_3^- concentrations observed higher in the water column. The somewhat lower values near the surface could be the result of either microbial assimilation of NH_4^+, denitrification as a result of water circulating back into the anaerobic zone, plant uptake, or dilution due to precipitation/snow melt on the wetland.

The 30cm samples from both PB2 and PB4 contain both NH_4^+ and NO_3^-. The only type of environment in which both species would be present is one where NH_4^+ is being oxidized to NO_3^-. While it may be the case that the interface between NH_4^+-enriched water and NO_3^--enriched water is at 30 cm in both locations, it is also possible that something peculiar to the samples is causing either transformation in the sample bottle or an erroneous result from the analytical equipment.

The presence of NH_4^+ at depth in the wetland is problematic, since no pathway exists to convert NO_3^- into NH_4^+. The groundwater surrounding, and presumably below, the wetland has been shown to be both aerobic and to contain NO_3^-, in concentrations ranging from near zero to over 10 ppm. The water flowing into the wetland has been shown to contain some (~2ppm) NO_3^-, but no detectable NH_4^+. There is virtually no observable overland flow into the wetland. So all potential physical pathways (overland, channel, and groundwater) have been examined and shown not to contribute NH_4^+ to the wetland. No chemical or microbial pathway exists to convert NO_3^-, which has been detected, into NH_4^+.

While there is no ‘smoking gun,’ in this case, there is at least one very strong possibility that may help explain the occurrence of NH_4^+ in the wetland, and the subsequent occurrence of NO_3^- in the outflow. Returning to the site description, recall that there is a large retention basin at the top of the slope, roughly due south of transect 5. The sites where NH_4^+ was detected in the waters above the aquiclude were all either on the south side of the wetland or along the long axis, and all between transects 3 through 7. Air photos of the site from the 1930's and 1970's reveal substantial erosion scars on the south side (Appendix B), and discussions with both the owner and Institute researchers indicate that the retention basin has failed at least once in the past. This basin was constructed in an attempt to slow the flow of water off the upper fields down into the wetland. Finally, recall that the area where mineral soils overlie muck, while somewhat broader, very closely conforms to the area where NH_4^+ has been found.

Therefore the most likely source of the NO_3^- observed flowing out of the wetland is the wetland itself, through the mineralization of a large quantity of organic N. This N is following the same general path outlined in the nitrogen cycle described in chapter 2, organic N mineralized to NH_4^+, then oxidized to NO_2^- and NO_3^-. Two obvious sources exist for the organic N present within the wetland. First, it may simply be organic residue associated with changes in landuse associated with settlement. Whereas the wetland developed within a forested environment over several thousand years, farming has, in the past hundred years, introduced radically different solar, hydrologic and nutrient regimes. These changes alone (warmer and drier today) might be adequate to cause the situation observed by modifying the balance between decomposition and nutrient uptake in such a way as to create a surplus of organic N.

A strong possibility also exists that the wetland received substantial direct inputs of manure and fertilizers over most of the last half-century. Any of these scenarios, or all three in conjunction (local environmental change, manure/fertilizers from fields, and manure from retention basin), are likely possible scenarios for developing a substantial reserve of organic N within the wetland.

The above results are summarized in an *in situ* nitrogen cycle diagram, Figure 27. Excess N fertilizers, primarily in organic form, are applied within zone 1, at B or B'. The organic N is converted by microbes within the unsaturated zone to NH_4^+, then to NO_2^- and NO_3^-. The NO_3^- is then translocated through the soil and into the underlying sand and gravel aquifer, C. The NO_3^- is then carried down gradient and eventually moves to some point off site, down gradient from the study site. This is the standard NO_3^- leaching/translocation model that has been observed and documented around the world (Freeze and Cherry, 1982; Kehew, 1996; Keeney, 1986). This nitrogen, while adversely impacting drinking water and possibly Donnell Lake, has no influence on the system in zone 2, above the aquiclude.

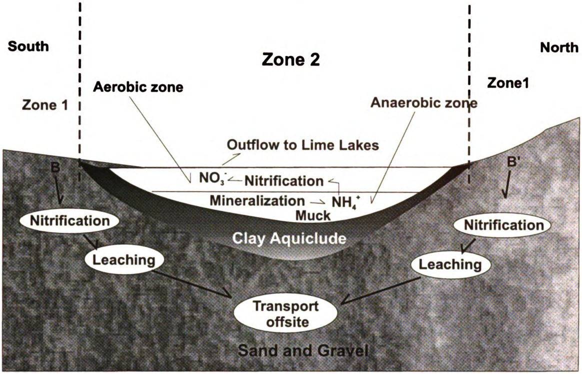

Figure 27: Idealized in situ N cycle within both the wetland and groundwater systems.

Most of the territory encompassed by zone 2 (Figure 27) is not farmed, and consequently is not directly fertilized. However, any N that is present in the mineral soils overlaying the muck may follow the path described in the previous paragraph, except that it would reach the wetland as NO_3^-, and be denitrified if it reached the anaerobic zone. This region also contains a substantial reserve of organic N of unknown origin, which is being decomposed to NH_4^+. This NH_4^+ eventually passes from the anaerobic zone to the aerobic zone, where it is exposed to an oxidizing environment and converted to either NO_2^- or NO_3^-. Once converted to NO_3^-, the N will be passed downstream with the outflow water from the wetland, and is observed as NO_3^- contamination in Lime Lakes and Donnell Lake.

Chapter 5

SUMMARY AND CONCLUSIONS

The study site, a small wetland in southwest Michigan, approximately 3 km (2 miles) west of Jones, has been observed to consistently contain nitrate (NO_3^-) in levels between 2 ppm and 10 ppm, the USEPA determined MCL for NO_3^-. Despite the land owners modified management practices, no improvement has been observed. Finally, water flowing into the wetland is lower in NO_3^- than water flowing out of the wetland, calling into question the role of wetlands as N sinks. The objective was to find the source of the N.

To accomplish the objective, methods were employed to separate potential sources and to evaluate the distribution of N within the wetland. Soils upslope from the wetland were sampled on a 30m grid to a depth of 1.5m and the samples analyzed for mineral N (NH_4^+ and NO_3^-). Piezometers were installed at 30m intervals along the perimeter of the wetland and samples analyzed for mineral N to monitor groundwater contributions. Piezometer nests were installed at 30m intervals inside the wetland to establish the vertical and horizontal distribution of mineral N within the wetland.

Physical exploration of the wetland and surrounding area with a screw auger revealed the presence of a gleyed layer of silty clay beneath the muck of the wetland. Later, measurements of hydraulic head in piezometers screened above and below the layer indicated that it acts as an aquiclude, effectively separating the saturated wetland muck from the groundwater within the sand and gravel aquifer below. The stream that is tributary to the wetland, however, may be fed by groundwater. Observations at the site indicated that there was no observable overland flow into the wetland proper or the tributary stream, probably due in part to the modified management practices employed by the farmer. Evidence does exist, both on air photos and in toeslope soil profiles, that erosion has occurred from the upslope fields into the wetland in the past.

Vertical profiling along the longitudinal axis of the wetland with the Hydrolab DataSonde 3 indicated the presence of aerobic and anaerobic layers within the wetland. However, these layers do not seem to be isolated: other parameters, such as temperature, specific conductance, and pH did not vary appreciably with depth. Consequently, water *is* circulating within the wetland. The microbial processes that remove oxygen from the water simply occur at a faster rate than the water mixes, resulting in the continuous removal of oxygen from waters entering the lower layer from the upper layer, thus maintaining an anaerobic zone.

In an anaerobic environment, NO_3^- is one of the first alternative oxidizers utilized by microbes. Similarly, NH_4^+ rarely exists very long in an aerobic environment before oxidizing. Thus, the redox conditions, and any vertical or horizontal variation in the redox conditions, within the wetland were crucial to this analysis. Further investigation and water sampling at multiple depths within the wetland revealed a NH_4^+ to NO_3^- gradient that corresponded directly to the DO gradient observed with the Hydrolab.

However, because the conversion from NH_4^+ to NO_3^- is non-reversible, and NH_4^+ is in the wetland, there must be a source for NH_4^+ within the wetland. A literature search and discussions with experts indicate that NH_4^+ is not susceptible to leaching under any circumstance. Even if leaching were occurring, it could only be happening in the area above the basin formed by the aquiclude, and virtually none of that receives fertilizer. Thus, based on the nitrogen cycle, the source must be organic N. Because organic N is typically a solid, translocation through the soil column does not occur. Thus, the organic N must already be within the wetland.

At least two possible explanations exist for how the organic N surplus came to reside in the wetland. The first invokes land use change. The transition from a forest to pasture and cropland following settlement unquestionably changed the nutrient budget of the wetland and the surrounding sub-watershed. However, it is unclear whether that is the sole cause. The second source is past runoff of manure from the upslope fields, perhaps combined with the failure of the retention basin used to slow runoff from fields further upslope. This retention basin undoubtedly filled with manure at times in the past, and the basin's failure could have deposited a substantial load of organic material in the wetland downslope. Even without the failure of the basin, simple erosion could have had much the same effect, though perhaps less dramatically. Recent modifications to landuse around the wetland have effectively stopped overland flow into the wetland.

Scientific context of this research

From the outset, this project was designed to explore, isolate, and evaluate potential sources of N to the wetland. In so doing, elements from several methods of analyzing wetlands were employed. Classical input-output studies are based on evaluating the wetland as a "black box," and simply quantifying inputs and outputs to determine the effectiveness of the wetland in retaining nutrients (Johnston, 1991).

In this input-output phase of the investigation, the project yielded an uncommon result; the wetland is a net source of N to the watershed. Very few other authors have found wetlands to be net sources of NO_3^-. Barsdate and Alexander (1975), working in a precipitation-driven tundra environment, found a situation where NH_4^+ was oxidizing to NO_3^-. However, all wetlands identified by Johnston (1991), in her comprehensive review of the nutrient retention in freshwater wetlands, were identified as nutrient sinks. Indeed, in two specific cases cited (Kadlec, 1983; Knight et al., 1987), direct inputs of sludge to wetlands did not decrease retention of N, though both of these studies were performed in warmer climates, which could impact the microbial processes of N transformation.

The input-output studies, and the vast majority of studies on natural wetlands, were thus of limited value in addressing this anomalous situation. However, some aspects, such as the vertical sampling scheme within the wetland, were drawn from both lacustrine research (D'Angelo and Reddy, 1993) and from the engineered wetland literature (Zhu and Sikora, 1995; Sikora et al. 1995). Constructed wetlands research has also been valuable in assessing some of the N transformations that have been observed at the study site. Cycling between aerobic and aerobic zones is a key management strategy to encourage nitrification, denitrification, and subsequent release of N from the constructed wetland to the atmosphere (Johnston, 1991). The natural wetland studied is following the nitrification pathway desired in constructed wetlands (Reed et al. 1988; Zhu and Sikora, 1995), including the 0.5 mg/L DO level required for nitrification of NH_4^+ to NO_3^- (Sikora et al. 1995). However, because of the lack of control at the study site (varied vegetation, uncontrolled inflows and outflows, indeterminate mixing patterns) the wetland is not suitable for the application of most of the methods employed to evaluate constructed wetlands.

Implications of this research

While the geological setting of this study is relatively unique to the glaciated upper Midwest, this pathway for NO_3^- to enter surface water systems has rarely, if ever been mentioned elsewhere in either the agronomy or water quality literature. The individual logical components have existed for years in the disciplines of agronomy (the N cycle) and in hydrology (aquicludes and DO gradients), yet the pieces of this complex pedo-hydrologic system have not before been forced by circumstance into combination. Similarly, this research demonstrates the applicability of constructed wetlands methods to better understanding natural wetlands with anthropogenic inputs of N.

Even though the theoretical components of this contamination process have been well known, the practical implications for future environmental remediation, management and research, both in the Donnell Lake region, and elsewhere, are substantial. First and foremost, this research emphasizes the importance of analyzing water samples for both NO_3^- and NH_4^+ rather than just NO_3^-, even though only NO_3^- is a direct threat to human health (Comly, 1945). The transformation between NH_4^+ and NO_3^- is so easily accomplished in aerobic environments that NH_4^+ might well be considered a threat by association. Thus, the importance of obtaining both NO_3^- and NH_4^+ data towards effectively understanding such a situation cannot be overemphasized; without data on both components there would have been no way to credibly construct the pathway described above.

In terms of management and remediation, this project emphasizes the significance of past events, both continuous, such as repeated over-application of manure, as well as singular instances of pollution, such as the failure of a retention basin. If the source of the organic N is in fact manure, we can be fairly confident that that manure was in place in the wetland five years ago, before the current land owner took possession. Using estimated land-applied sludge decomposition rates (Jacobs, 1997), it could take two to three *decades* to clear the watershed of excess N. And in the intervening period, N release rates would decline asymptotically. Thus, a one-time over-application or the failure of an upslope retention basin would not only result in much higher nitrogen loadings the first season, but also in higher than normal loadings for years into the future. The only effective way to remediate this situation would be to excavate the material, which would be costly, difficult, and could potentially release more N downstream as a result of the disturbance. In short, the situation in this particular wetland underscores the importance of riparian buffers and proper management practices at all times. A long term problem can be created in a very short period of time.

Future Research

As is often the case, just as scientific research answers questions, it poses more. For instance, what *exactly* is the source of the N in the wetland? This question might be addressed through the use of N or C isotope analyses to associate the N with an animal (manure) or vegetable (decomposition of muck due to environmental change) source (Blackburn and Knowles, 1993; Coleman and Frey, 1991).

Another intriguing possibility is that, in an environment such as this one, with sandy soils and high fertilizer applications, NH_4^+ *might actually leach*. While NH_4^+ leaching was not observed and is probably not contributing to NH_4^+ in the wetland itself, if the potential exists anywhere, it exists in environments like the Donnell Lake watershed, especially in toeslope settings where the water table is near the surface. Translocation of NH_4^+ could potentially be every bit as important as that of NO_3^-, because both will eventually pose the same threat in aerated environments.

Finally, from a methodological standpoint, this study site poses some interesting problems for quantifying the N transformations occurring. While application of input-output analyses are useful to a point, a more thorough understanding of the processes within the wetland is required to manage, and possibly remediate, the situation. Unlike constructed wetlands, with absolutely impermeable boundaries, known dimensions, and controlled circulation, this natural wetland probably has none of these attributes. And unlike the microcosm studies carried out on sediment cores (e.g. D'Angelo and Reddy, 1993), operating out in the elements, with varying sunshine, precipitation, wind, temperature, and vegetation introduces an assortment of new challenges, not the least of which are the challenges of maintaining equipment and sample integrity. More directed study and development of techniques for monitoring *in situ* conditions with the precision as in the laboratory are crucial to gaining a proper understanding of what is actually occurring in the environment.

Nitrogen, while one of the longest studied elements in the environment, continues to be a subject of research because it is a source of concern. Nitrogen can be both a threat to human health and contribute to the fouling of lakes and rivers by eutrophication. However, unlike many other materials, nitrogen is crucial to nearly all living organisms, including humans beings, the crops we eat, and the livestock we consume. Consequently, our choice should be to better understand the role of nitrogen in the environment, and better educate as to the hazards associated with this basic element of life.

APPENDIX A

LOCATION KALAMAZOO MI+IN WI

Established Series
Rev. NWS-LWB-WEF
6/92

KALAMAZOO SERIES

The Kalamazoo series consists of very deep, well drained soils formed in loamy outwash overlying sand, loamy sand, or sand and gravel
outwash on outwash plains, terraces, valley trains, and low lying moraines. These soils have moderate permeability in the upper loamy materials
and rapid permeability in the lower sandy materials. Slopes range from 0 to 18 percent. Mean annual precipitation is about 34 inches, and mean
annual temperature is about 49 degrees F.

TAXONOMIC CLASS: Fine-loamy, mixed, mesic Typic Hapludalfs

TYPICAL PEDON: Kalamazoo loam - on a 1 percent slope in a cultivated field. (Colors are for moist soil unless otherwise stated.)

Ap--0 to 11 inches; dark grayish brown (10YR 4/2) loam; light brownish gray (10YR 6/2) dry; weak medium granular structure; friable;
common fine roots; neutral; abrupt smooth boundary. (6 to 11 inches thick)

Bw--11 to 16 inches; dark yellowish brown (10YR 4/4) loam; weak medium subangular blocky structure; friable; common fine roots; dark
grayish brown (10YR 4/2) material in pores and wormholes; neutral; gradual wavy boundary. (0 to 6 inches thick)

Bt1--16 to 20 inches; dark yellowish brown (10YR 4/4) clay loam; moderate medium subangular blocky structure; firm; thin continuous dark
yellowish brown (10YR 3/4) clay films on faces of peds; few fine roots; 1 percent gravel; neutral; gradual wavy boundary.

Bt2--20 to 30 inches; dark brown (7.5YR 4/4) clay loam; moderate medium subangular blocky structure; firm; thin continuous dark yellowish
brown (10YR 3/4) clay films on faces of peds; few fine roots; about 1 percent gravel; neutral; gradual wavy boundary. (The combined
thickness of the Bt1 and Bt2 horizons ranges from 8 to 30 inches.)

Bt3--30 to 38 inches; dark yellowish brown (10YR 4/4) sandy loam; weak medium subangular blocky structure; friable; thin discontinuous dark yellowish brown (10YR 3/4) clay films on faces of peds; about 5 percent gravel; moderately acid; gradual wavy boundary. (5 to 15 inches thick)

2BC1--38 to 42 inches; dark yellowish brown (10YR 4/6) loamy coarse sand; massive; friable; about 10 percent gravel; moderately acid; gradual wavy boundary.

2BC2--42 to 55 inches; dark yellowish brown (10YR 4/4) gravelly loamy sand; massive; friable; about 20 percent gravel; neutral; gradual wavy boundary.

2C--55 to 60 inches; dark yellowish brown (10YR 4/4) gravelly sand; single grain; loose; about 20 percent gravel; slight effervescence; slightly alkaline.

TYPE LOCATION: Kalamazoo County, Michigan; about 1 mile south and 4 miles west of the village of Scotts; 115 feet east and 635 feet north of the southwest corner, sec. 28, T. 3 S., R. 10 W.

RANGE IN CHARACTERISTICS: Solum thickness and depth to calcareous material ranges from 40 to 60 inches. The depth to the sandy discontinuity ranges from 25 to 40 inches. Reaction ranges from strongly acid to neutral above the calcareous material. Coarse fragments range from 0 to 20 percent by volume in the solum.

The Ap horizon has hue of 10YR or 7.5YR, value of 3 to 5, and chroma of 2 or 3. Uncultivated areas have an A horizon, 2 to 6 inches thick, that has hue of 10YR, value of 3 or 4, and chroma of 2 or 3. Some pedons have an E horizon, 1 to 6 inches thick, that has hue of 10YR or 7.5YR, value of 4 or 5, and chroma of 2 or 3. The A and E horizons are loam, silt loam, or sandy loam.

The Bt horizons have hue of 10YR, 7.5YR, or 5YR, value of 3 or 4, and chroma of 2 to 4. They are clay loam, sandy clay loam, loam, sandy loam, or gravelly analogues of these textures. The upper 20 inches of the argillic horizon averages between 18 and 35 percent clay but is predominantly about 27 percent. The lower part of the argillic is coarse-loamy material greater than 5 inches thick.

The 2BC horizons have hue of 10YR, 7.5YR, or 5YR, value of 3 to 6, and chroma of 2 to 6. They are loamy sand, loamy coarse sand, or sand with gravelly or very gravelly analogues of these textures. Some pedons have thin bands of sandy loam. The lower part is slightly alkaline in some pedons.

The 2C horizon has hue of 10YR or 7.5YR, value of 4 to 6, and chroma of 3 to 6. It is sand, coarse sand, gravelly sand, or stratified sand and gravel. Some pedons have thin bands of loamy sand or sandy loam. Gravel content ranges from 0 to 60 percent by volume. It is slightly or moderately alkaline.

COMPETING SERIES: These are the Amanda, Belmont, Belmore, Chenult, Chili, Coggon, Conestoga, Douds, El Dara, Gallman, Grellton, Hayden, Hebron, Hickory, High Gap, Hollinger, Kanawha, Kendallville, Kidder, Kosciusko, LeRoy, Letort, Lindley, Mandeville, Martinsville, McHenry, Miami, Mifflin, Military, Nodine, Norden, Ockley, Owosso, Pecatonica, Princeton, Rainsville, Rawson, Relay, Renova, Richland, Riddles, Sisson, Skelton, Strawn, Summitville, Theresa, Wawasee, Westville, Whalan, Woodbine, and Wykoff series. The Amanda, Belmont, Chenault, Coggon, Conestoga, Douds, El Dara, Gallman, Grellton, Hayden, Hebron, Hickory, High Gap, Hollinger, Kanawha, Kidder, LeRoy, Letort, Lindley, Mandeville, Martinsville, McHenry, Miami, Mifflin, Military, Nodine, Norden, Owosso, Pecatonica, Rainsville, Rawson, Relay, Renova, Richland, Riddles, Roseville, Sisson, Skelton, Strawn, Summitville, Theresa, Wawasee, Westville, Whalan, Woodbine, and Wykoff soils do not have loamy sand or coarser textures within a depth of 60 inches. Belmore soils have silt loam and sandy loam strata in the C horizon. Chili soils do not contain free carbonates within depths of 60 inches. Kendallville soils have loam or clay loam till within a depth of 60 inches. Kosciusko soils contain more than 20 percent gravel in the solum. Ockley soils do not have gravelly loamy sand or loamy sand within 40 inches. Princeton soils have C horizons of very fine sand, fine sand, or silt.

GEOGRAPHIC SETTING: Kalamazoo soils formed in loamy outwash overlying sand, loamy sand, or sand and gravel outwash on outwash plains, terraces, valley trains, and low lying moraines. Slope gradients range from 0 to 18 percent. Mean annual precipitation ranges from 29 to 37 inches and mean annual temperature from 47 to 53 degrees F.

GEOGRAPHICALLY ASSOCIATED SOILS: These are the Boyer, Dowagiac, Matherton, Oshtemo, Sebewa, Sunfield, and Volinia soils. Moderately well drained Sunfield, somewhat poorly drained Matherton, and very poorly drained Sebewa soils are the most common associates. Also associated are the Volinia and Dowagiac soils which are Mollisols. The coarser textured Oshtemo and Boyer are associated in some areas.

DRAINAGE AND PERMEABILITY: Well drained. Runoff is slow on the level areas and rapid on the steeper slopes. Permeability is moderate in the upper loamy materials and rapid in the lower sandy materials.

USE AND VEGETATION: A large part is cropped to corn, wheat, soybeans, and hay. A small part is in pasture. Some areas adjacent to the larger cities are idle cropland. The native vegetation was northern red oak and hickory forests.

DISTRIBUTION AND EXTENT: Southern Michigan and northern Indiana. The series is of large extent.

MLRA OFFICE RESPONSIBLE: Indianapolis, Indiana

SERIES ESTABLISHED: Kalamazoo County, Michigan, 1978.

REMARKS: Diagnostic horizons and features recognized in this pedon are: ochric epipedon - the zone from the surface to 11 inches (Ap horizon); argillic horizon - the zone from 16 to 38 inches (Bt1, Bt2, and Bt3 horizons).

National Cooperative Soil Survey
U.S.A.

LOCATION OSHTEMO MI+IN OH WI

Established Series
Rev. NWS-LWB-TWH
6/95

OSHTEMO SERIES

The Oshtemo series consists of very deep, well drained soils formed in loamy and sandy glacial drift on outwash plains, valley trains, moraines, and beach ridges. Permeability is moderately rapid in the upper loamy materials and very rapid in the lower sandy materials. Slopes range from 0 to 55 percent. Mean annual precipitation is about 33 inches, and mean annual temperature is about 50 degrees F.

TAXONOMIC CLASS: Coarse-loamy, mixed, mesic Typic Hapludalfs

TYPICAL PEDON: Oshtemo sandy loam on a 4 percent slope in a cultivated field. (Colors are for moist soil unless otherwise stated.)

Ap--0 to 9 inches; dark grayish brown (10YR 4/2) sandy loam, light brownish gray (10YR 6/2) dry; weak coarse granular structure; very friable; slightly acid; abrupt smooth boundary. (7 to 12 inches thick)

E--9 to 14 inches; brown (10YR 5/3) sandy loam, light brownish gray (10YR 6/2) dry; weak fine subangular blocky structure; very friable; many worm and root channels filled with Ap material; about 3 percent fine gravel; moderately acid; clear wavy boundary. (0 to 12 inches thick)

Bt1--14 to 26 inches; dark reddish brown (5YR 3/4) sandy loam, dark brown (7.5YR 4/4) dry; weak coarse subangular blocky structure; friable; faint discontinuous clay films on faces of peds; about 8 percent gravel; strongly acid; clear wavy boundary.

Bt2--26 to 35 inches; dark brown (7.5YR 4/4) sandy loam; weak coarse subangular blocky structure; friable; few dark brown (7.5YR 3/2) masses 1 to 3 inches in diameter; faint discontinuous clay films on faces of peds; some clay bridging between sand grains and small gravel; about 5 percent gravel; strongly acid; gradual wavy boundary. (The combined thickness of the Bt horizons is 8 to 35 inches.)

2BC1--35 to 46 inches; dark brown (7.5YR 4/4) loamy sand; many dark brown (7.5YR 3/2) spots and masses up to 2 inches in diameter; single grain; loose; about 5 percent gravel; moderately acid; diffuse irregular boundary.

2BC2--46 to 60 inches; dark brown (7.5YR 4/4) loamy sand; dark brown (7.5YR 3/2) discontinuous bands 1/8 inch thick; most sand grains have dark brown (7.5YR 3/2) coatings; single grain; loose; moderately acid; abrupt irregular boundary. (The combined thickness of the 2BC horizons is 0 to 30 inches.)

2C--60 to 66 inches; grayish brown (10YR 5/2) stratified sand and gravelly sand; single grain; loose; about 20 percent gravel; some thin lime coatings on lower side of some gravel; strongly effervescent; moderately alkaline.

TYPE LOCATION: St. Joseph County, Michigan; about 1 mile north of Centreville; 800 feet north and 880 feet east of the southwest corner, sec. 18, T. 6 S., R. 10 W.

RANGE IN CHARACTERISTICS: Depth to the base of the argillic horizon is 20 to 40 inches. Solum thickness ranges from 40 to 75 inches. The depth to calcium carbonates ranges from 40 to 70 inches. Coarse fragment content is 1 to 30 percent in the A, E, Bt, and 2BC horizons. Mean annual soil temperature is 49 to 54 degrees F.

The Ap horizon has hue of 10YR or 7.5YR, value of 3 to 5 moist, and chroma of 2 or 3, moist or dry. Texture is loam, sandy loam, fine sandy loam, loamy sand, or loamy fine sand. Reaction is strongly acid to neutral.

The E horizon has value of 5 or 6 moist, and chroma of 3 to 6, moist or dry. Texture is loam, sandy loam, fine sandy loam, loamy sand, or loamy fine sand. Reaction is strongly acid to neutral.

The Bt horizon has hue of 5YR, 7.5YR, or 10YR; value of 3 to 5; and chroma of 3 to 6. Texture is sandy loam, gravelly sandy loam, sandy clay loam, gravelly sandy clay loam, or fine sandy loam. Clay content averages 10 to 18 percent. In the lower part of the solum, in some pedons, the Bt horizon is in bands 1/8 to 4 inches thick separated by sand or loamy sand. In some pedons the lower Bt horizon is coarse sandy loam. Reaction is strongly acid to slightly acid in the upper part and strongly acid to neutral in the lower part.

The 2BC horizon has hue of 5YR, 7.5YR, or 10YR; value of 3 to 5; and chroma of 2 to 6. Texture is loamy sand, sandy loam, gravelly loamy sand, or gravelly sandy loam. Reaction is strongly acid to neutral.

The 2C horizon has value of 5 or 6, and chroma of 2 to 6. Textures are stratified and dominantly sand and gravel or loamy sand or loamy coarse sand. Gravel content averages 10 to 50 percent. Some pedons have clayey or loamy substratums below 60 inches. Reaction is slightly alkaline or moderately alkaline.

COMPETING SERIES: These are the Alvin, Boyer, Brownsburg(T), Burnsville, Council, Dryden, Eleva, Elmdale, Hillsdale, Lamont, Lapeer, Mecan, Perrin, and Wyocena series. Alvin soils have less than 1 percent coarse fragments and greater than 50 percent very fine and fine sand in the lower control section. Boyer soils have carbonates above 40 inches. Brownsburg soils have a lithic contact in the lower part of the control section. Burnsville soils have less than 45 percent fine or coarser sand in the solum. Council, Dryden, Elmdale, Hillsdale, Lamont, Lapeer, and Mecan soils do not have sandy textures within a depth of 40 inches. Eleva soils have a paralithic contact in the control section. Perrin soils have redox depletions in the lower part of the Bt horizon. Wyocena soils have sola less than 40 inches thick and are not stratified below 40 inches.

GEOGRAPHIC SETTING: Oshtemo soils are on outwash plains, valley trains, moraines, and beach ridges. Slopes range from 0 to 55 percent. Elevations are 540 to 1,000 feet. The Oshtemo soils formed in loamy and sandy glacial drift that has a high content of quartz and contains variable amounts of material derived from igneous and metamorphic rocks, sandstone, limestone, and dolomite. Mean annual precipitation ranges from 28 to 36 inches, and the mean annual temperature ranges from 47 to 52 degrees F. The frost free period is 120 to 180 days.

GEOGRAPHICALLY ASSOCIATED SOILS: These are the competing Boyer and Hillsdale series, and the Bronson, Brady, Gilford, Kalamazoo, and Spinks soils. The Bronson, Brady, and Gilford soils have zones of aquic conditions and are in a drainage sequence with the Oshtemo soils. Boyer, Spinks, and Kalamazoo soils are associated on outwash plains and valley trains. Spinks and Hillsdale soils are closely associated with Oshtemo on moraines. Spinks soils have argillic horizons composed of lamellae and Kalamazoo soils contain from 18 to 35 percent clay in the argillic horizon.

DRAINAGE AND PERMEABILITY: Well drained. Surface runoff is very slow to medium depending upon slopes. Permeability is moderately rapid in the upper part and very rapid in the lower part.

USE AND VEGETATION: The soils are cultivated in most areas. The principal crops are small grains, soybeans, corn, and hay. The remainder is in forest or permanent pasture. The original vegetation was hardwood forest of oak, hickory, and sugar maple.

DISTRIBUTION AND EXTENT: Southern Michigan, northern Indiana, southeastern Wisconsin, and northern Ohio. The series is of large extent.

MLRA OFFICE RESPONSIBLE: Indianapolis, Indiana

SERIES ESTABLISHED: Kalamazoo County, Michigan, 1922.

REMARKS: Diagnostic horizons and features recognized in this pedon are: Ochric epipedon - from the surface to 9 inches (Ap horizon).
Argillic horizon - from 14 to 35 inches (Bt1 and Bt2 horizons). Particle-size control section - the zone from 14 to 34 inches (Bt1 and most of the Bt2 horizon). Udic soil moisture regime.

National Cooperative Soil Survey
U.S.A.

LOCATION BRADY MI+IA IN OH

Established Series
Rev. LWB-WEF
4/96

BRADY SERIES

The Brady series consists of very deep, somewhat poorly drained soils formed in loamy glacial drift overlying sand or gravelly coarse sand outwash materials on outwash plains, valley trains, terraces and lake plains. These soils have moderately rapid permeability. Slopes range from 0 to 6 percent. Mean annual precipitation is about 34 inches, and mean annual temperature is about 49 degrees F.

TAXONOMIC CLASS: Coarse-loamy, mixed, mesic Aquollic Hapludalfs

TYPICAL PEDON: Brady sandy loam - on a 1 percent slope in a cultivated field. (Colors are for moist soil unless otherwise stated.)

Ap--0 to 9 inches; very dark grayish brown (10YR 3/2) sandy loam, grayish brown (10YR 5/2) dry; moderate medium granular structure; friable; slightly acid; abrupt smooth boundary. (7 to 9 inches thick)

E--9 to 13 inches; grayish brown (10YR 5/2) sandy loam; weak coarse granular structure; friable; few fine distinct yellowish brown (10YR 5/6) accumulations of iron oxide; slightly acid; clear wavy boundary. (0 to 6 inches thick)

BE--13 to 23 inches; brown (10YR 5/3) sandy loam; weak coarse subangular blocky structure; friable; many medium distinct gray (10YR 5/1) iron depleations; moderately acid; clear wavy boundary. (0 to 14 inches thick)

Bt--23 to 37 inches; dark yellowish brown (10YR 4/4) sandy loam; moderate medium subangular blocky structure; friable; few faint clay films on faces of peds and bridging of sand grains; very dark grayish brown (10YR 3/2) sandy loam worm casts and fillings in root channels; many medium distinct gray (10YR 5/1) iron depleations and yellowish brown (10YR 5/8) iron oxide accumulations; about 6 percent gravel; moderately acid; abrupt irregular boundary. (8 to 20 inches thick)

BC--37 to 56 inches; dark brown (7.5YR 4/4) loamy sand; weak coarse subangular blocky structure; very friable; few thin 1/8 to 2 inch thick discontinuous dark brown (7.5YR 4/4) sandy loam layers; few medium distinct gray (10YR 5/1) iron depleations and yellowish brown (10YR

5/8) iron oxide accumulations; neutral; abrupt irregular boundary. (0 to 24 inches thick)

2C--56 to 60 inches; brown (10YR 5/3) gravelly coarse sand, single grain; loose; common medium distinct gray (10YR 5/1) iron depleations; about 15 percent gravel; slightly effervescent; slightly alkaline.

TYPE LOCATION: Eaton County, Michigan; about 3 miles southwest of the town of Charlotte, 800 feet east and 500 feet north of center of sec. 33, T. 2 N., R. 5 W.

RANGE IN CHARACTERISTICS: The thickness of the solum ranges from 36 to 70 inches and depth to free carbonates ranges from 40 to 70 inches. The solum ranges from neutral to strongly acid. Rock fragments range from 0 to 25 percent by volume throughout the solum.

The Ap horizon has hue of7.5YR or 10YR, value of 2 or 3, and chroma of 1 to 3. The E horizon has hue of 10YR, value of 5 or 6, and chroma of 2 or 4. The A and E horizons are sandy loam, fine sandy loam, loamy fine sand, or loamy sand, and less commonly loam or silt loam.

The B horizon has hue of 10YR or 7.5YR, value of 4 to 6, and chroma of 3 to 6. The argillic horizon commonly has mottles with chroma of 2 or less and value of 4 or more throughout. It commonly is sandy loam or gravelly sandy loam and less commonly sandy clay loam, gravelly sandy clay loam, or clay loam. Where the texture is sandy clay loam or clay loam, the layer is less than 8 inches thick. The BC horizon has hue of 7.5YR or 10YR, value of 4 to 7, and chroma of 2 to 6. It is sandy loam or loamy sand.

The 2C horizon has hue of 10YR, value of 4 to 6, and chroma of 1 to 4. It is gravelly coarse sand, coarse sand, sand,gravelly sand, very gravelly sand or stratified coarse sand and gravel. Rock fragments range from 10 to 55 percent by volume. It ranges from neutral to moderately alkaline.

COMPETING SERIES: These are the Dixboro, Oakton and Wasepi series, and the similar Bronson and Matherton soils. Dixboro soils are underlain at depths less than 40 inches by stratified very fine sand and silt loam. Oakton soils contain less than 10 percent coarse fragments at depths of 40 to 60 inches. Wasepi soils have free carbonates within depths of 40 inches. Bronson soils have a surface layer that has value of 6 or more dry and do not have low chroma mottles in the upper 4 to 8 inches of the argillic horizon. Matherton soils are fine-loamy.

GEOGRAPHIC SETTING: Brady soils formed in loamy glacial drift overlying sand or gravelly coarse sand outwash materials on outwash plains, valley trains, terraces and lake plains. Slope gradients are dominantly 0 to 2 percent and range from 0 to 6 percent. Mean annual precipitation ranges from 29 to 37 inches. The mean annual temperature is about 47 to 54 degrees F.

GEOGRAPHICALLY ASSOCIATED SOILS: These are the competing Bronson and Wasepi soils and the Boyer, Gilford, Oshtemo, and Perrin soils. Boyer and Perrin soils are on nearby higher landscape positions. Boyer soils are well drained, and Perrin soils are moderately well drained. Brady soils are in a drainage sequence with the very poorly drained Gilford and the well drained Oshtemo soils.

DRAINAGE AND PERMEABILTY: Somewhat poorly drained. Ths soil has a seasonal high water table that ranges from .5 to 1.5 feet below the surface from November to May. Surface runoff is very slow or slow. Permeability is moderately rapid.

USE AND VEGETATION: A large part is under cultivation. Where drainage is adequate it is cropped to corn, small grain, beans, and bromegrass-alfalfa hay. A small part is in permanent pasture or forest. The native vegetation was deciduous forest.

DISTRIBUTION AND EXTENT: Southern Michigan, northern Indiana, northwestern Ohio, and eastern Iowa. The series is of large extent.

MLRA OFFICE RESPONSIBLE: Indianapolis, Indiana

SERIES ESTABLISHED: Van Buren County, Michigan, 1922. REMARKS: Diagnostic horizons and features recognized in this pedon are: ochric epipedon - too thin for mollic (9 inches); argillic horizon - the zone from 23 to 37 inches (Bt horizon); udic features - udic moisture regime; aquic features - mottles with chromas of 2 or less in upper 10 inches of the argillic horizon and are saturated in that horizon; mollic intergrade - Ap horizon has value of 3 moist and 5 dry.

ADDITIONAL DATA: Soil Interpretation Record No.- MI0025

National Cooperative Soil Survey
U.S.A.

LOCATION ADRIAN MI+CT IA IL IN MN NJ NY OH RI VT WI

Established Series
Rev. RWJ-WEF-TWH
6/95

ADRIAN SERIES

The Adrian series consists of very deep, very poorly drained soils in depressions on outwash plains, lake plains and terraces, floodplains, moraines, and till plains. The soils formed in herbaceous organic material and in the underlying sandy deposits. Permeability is moderately slow to moderately rapid in the organic material and rapid in the sandy material. Slopes range from 0 to 2 percent. Mean annual precipitation is about 32 inches, and mean annual temperature is about 48 degrees F.

TAXONOMIC CLASS: Sandy or sandy-skeletal, mixed, euic, mesic Terric Medisaprists

TYPICAL PEDON: Adrian muck - on a 1 percent slope under marsh vegetation. (Colors are for moist soil unless otherwise stated.)

Oa1--0 to 16 inches; black (10YR 2/1) broken face, black (N 2/0) rubbed muck; about 12 percent fiber, less than 5 percent rubbed; moderate medium granular structure; primarily herbaceous fibers; neutral (pH 7.0 in water); abrupt wavy boundary.

Oa2--16 to 20 inches; black (10YR 2/1) broken face, very dark brown (10YR 2/2) rubbed muck; about 15 percent fibers, less than 5 percent rubbed; weak coarse subangular blocky structure; primarily herbaceous fibers; slightly acid (pH 6.5 in water); gradual wavy boundary.

Oa3--20 to 27 inches; black (10YR 2/1) broken face, black (10YR 2/1) rubbed muck; about 12 percent fibers, less than 5 percent rubbed; weak thick platy structure; primarily herbaceous fibers; moderately acid (pH 6.0 in water); gradual wavy boundary.

Oa4--27 to 34 inches; black (10YR 2/1) broken face, black (10YR 2/1) rubbed muck; about 12 percent fibers, less than 5 percent rubbed; massive; primarily herbaceous fibers; strongly acid (pH 5.5 in water); abrupt smooth boundary. (Combined thickness of the Oa horizons is 16 to 51 inches)

C--34 to 60 inches; gray (10YR 5/1) sand; single grain; loose; strongly effervescent; common medium prominent light olive brown (2.5Y 5/4) masses of iron accumulation; moderately alkaline.

TYPE LOCATION: Gratiot County, Michigan; about 1 1/2 miles southeast of the village of Ashley; 1,020 feet north and 100 feet east of the southwest corner, sec. 16, T. 9 N., R. 1 W.

RANGE IN CHARACTERISTICS: The difference between mean summer and mean winter soil temperature is 17 to 25 degrees F. or more. The depth to the sandy C horizon ranges from 16 to 51 inches. The organic fibers are derived primarily from herbaceous plants, but some layers contain as much as 50 percent material of wood origin.

The surface tier has hue of 10YR to 5YR, or is neutral; value of 2; and chroma of 0 to 3. It is dominantly muck (sapric material); however, some pedons have mucky peat (hemic material). Some pedons have a thin mat, 1 to 4 inches thick, of sphagnum moss on the surface. Reaction is strongly acid to neutral.

The subsurface and bottom tiers have hue of 10YR to 5YR, or is neutral; value of 2 or 3; and chroma of 0 to 3. Thin layers, less than 10 inches thick, of mucky peat (hemic material) are in some pedons. Thin layers, less than 5 inches thick, of peat (fibric material) are in some pedons. In some pedons a sedimentary peat layer 1 to 2 inches thick is present above the C horizon. Reaction is strongly acid to neutral.

The C horizon has hue of 5YR to 5Y, value of 2 to 6, and chroma of 1 to 4, or is neutral with value of 2 to 6. Texture is sand, coarse sand, fine sand, loamy sand, gravelly sand, or gravelly loamy sand. Gravel content is 0 to 25 percent. Strata of finer textures occur in some pedons. Reaction is slightly acid to moderately alkaline. This horizon is effervescent in some pedons.

COMPETING SERIES: This is the Fishtrap series. Similar soils are the Markey, Palms, Tawas, and Willette series. Fishtrap soils have a difference of less than 16 degrees F between mean summer and mean winter soil temperatures. Markey, and Tawas soils are frigid. Palms soils have loamy textures above 51 inches. Willette soils have clayey textures above 51 inches.

GEOGRAPHIC SETTING: Adrian soils occupy shallow closed depressions primarily on outwash plains, lake plains, lake terraces and floodplains, but can occur within moraines and till plains. Areas range from a few acres to several hundred acres in size. Slope gradients are 0 to 2 percent. Usually adjacent upland soils are sandy. Elevations are 600 to 1400 feet. The mean annual precipitation ranges from 29 to 45 inches, and the mean annual temperature ranges from 47 to 52 degrees F. The frost free period is 120 to 180 days.

GEOGRAPHICALLY ASSOCIATED SOILS: These are the Houghton and Granby soils. Houghton soils formed in herbaceous organic deposits more than 51 inches thick and are the most common associate. Granby soils are sandy throughout, and are generally are at the margins of the depressions.

DRAINAGE AND PERMEABILITY: Very poorly drained. The depth to the seasonal high water table ranges from 1 foot above the surface to 1 foot below the surface from November to May. Some areas are subject to frequent long periods of flooding from October through June. Surface runoff is very slow or ponded. Permeability is moderately slow to moderately rapid in the organic material and rapid in the sandy material.

USE AND VEGETATION: Most of this soil is in native vegetation. Much of it is in marsh grasses including sedges, reeds, grasses, and shrubs such as willow, alder, quaking aspen, and dogwood. Some areas have been drained to various degrees and are used for hay and pasture. A small proportion is used for cropland. Common crops include corn and truck crops.

DISTRIBUTION AND EXTENT: The southern part of lower Michigan, Connecticut, Iowa, Illinois, Indiana, Minnesota, New York, New Jersey, Ohio, Rhode Island, Vermont, and Wisconsin. The series is of large extent.

MLRA OFFICE RESPONSIBLE: Indianapolis, Indiana

SERIES ESTABLISHED: Sanilac County, Michigan, 1955.

REMARKS: Diagnostic horizons and features recognized in this pedon are: Sapric material - from the surface to 34 inches (Oa1, Oa2, Oa3 and Oa4 horizons).
Terric feature - mineral material in the zone from 34 to 60 inches (C horizon).

National Cooperative Soil Survey
U.S.A.

APPENDIX B

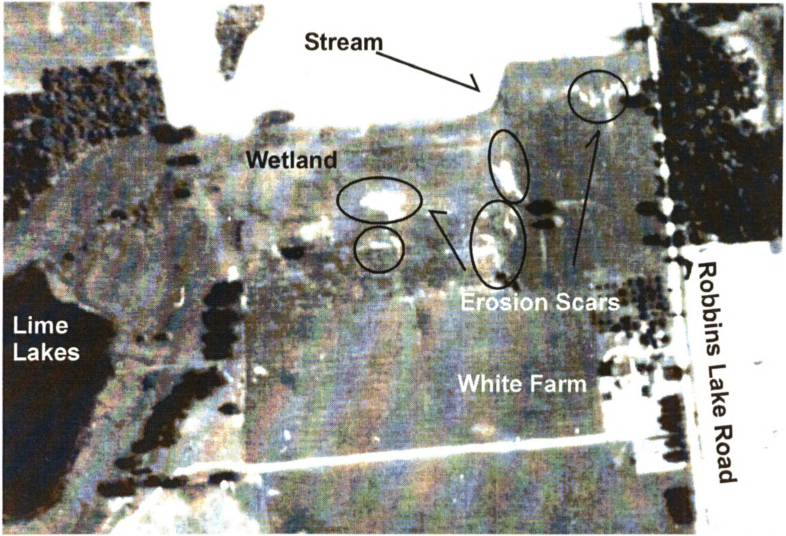

Figure 28: Aerial photograph of the study site from 1938. Notice the exposed earth, both in patches on the south side of the wetland and in the plowed fields north of the wetland and to the east of Robbins Lake Road.

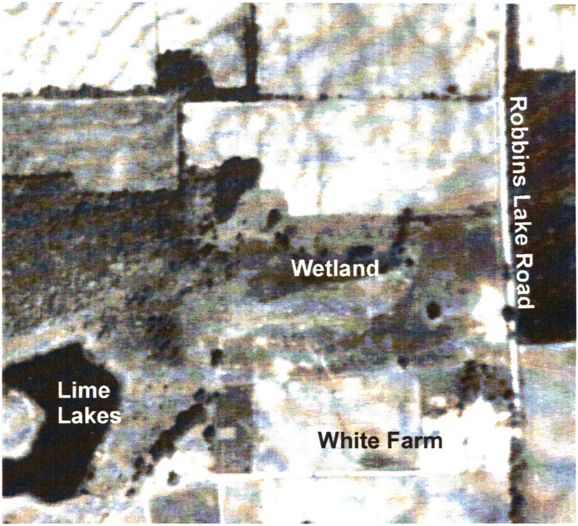

Figure 29: Aerial photograph of the study site in 1974.

Appendix B

APPENDIX C

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
NA2	1	30	0.12	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NA2	2	60	0.17	0.00	0.00	1.75	10.42	0.0	7.9	0.0	8.9	7.9	8.9
NA2	3	90	0.10	0.00	0.00	1.63	16.52	0.0	7.3	0.0	8.2	7.3	8.2
NA2	4	120	0.07	0.00	0.00	2.50	38.12	0.0	11.2	0.0	12.6	11.2	12.6
NA2	5	150	0.07	1.33	0.09	0.36	5.30	0.4	1.6	0.5	1.8	2.0	2.3
NA4	1	30	0.07	2.65	0.20	0.60	7.95	0.9	2.7	1.0	3.0	3.6	4.0
NA4	2	60	0.10	3.09	0.32	1.48	14.43	1.4	6.7	1.6	7.5	8.1	9.1
NA4	3	90	0.09	2.15	0.20	0.49	5.37	0.9	2.2	1.0	2.5	3.1	3.5
NA4	4	120	0.12	1.94	0.23	0.68	5.83	1.0	3.0	1.1	3.4	4.1	4.6
NA4	5	150	0.13	0.89	0.11	1.37	10.65	0.5	6.2	0.6	6.9	6.7	7.5
NA5	1	30	0.10	1.94	0.20	1.41	13.60	0.9	6.3	1.0	7.1	7.2	8.1
NA5	2	60	0.14	1.51	0.22	1.95	13.61	1.0	8.8	1.1	9.9	9.8	11.0
NA5	3	90	0.12	1.94	0.23	0.68	5.83	1.0	3.0	1.1	3.4	4.1	4.6
NA5	4	120	0.09	1.20	0.10	0.83	9.60	0.5	3.7	0.5	4.2	4.2	4.7
NA5	5	150	0.07	2.72	0.18	0.80	12.25	0.8	3.6	0.9	4.1	4.4	5.0
NA7	1	30	0.09	0.00	0.00	0.49	5.73	0.0	2.2	0.0	2.5	2.2	2.5
NA7	2	60	0.11	0.00	0.00	0.58	5.42	0.0	2.6	0.0	2.9	2.6	2.9
NA7	3	90	0.12	0.00	0.00	0.59	4.98	0.0	2.6	0.0	3.0	2.6	3.0
NA7	4	120	0.10	0.00	0.00	0.38	3.89	0.0	1.7	0.0	1.9	1.7	1.9
NA7	5	150	0.05	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NA8	1	30	0.10	0.00	0.00	0.29	2.76	0.0	1.3	0.0	1.5	1.3	1.5
NA8	2	60	0.13	0.00	0.00	0.91	6.86	0.0	4.1	0.0	4.6	4.1	4.6
NA8	3	90	0.18	0.00	0.00	0.54	3.03	0.0	2.4	0.0	2.8	2.4	2.8
NA8	4	120	0.16	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NA8	5	150	0.06	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB2	1	30	0.22	1.42	0.31	1.56	7.09	1.4	7.0	1.6	7.9	8.4	9.4
NB2	2	60	0.18	0.00	0.00	1.68	9.25	0.0	7.6	0.0	8.5	7.6	8.5
NB2	3	90	0.14	0.00	0.00	3.34	24.11	0.0	15.0	0.0	16.9	15.0	16.9
NB2	4	120	0.08	0.00	0.00	2.72	35.96	0.0	12.3	0.0	13.8	12.3	13.8
NB2	5	150	0.10	0.00	0.00	2.35	23.70	0.0	10.6	0.0	11.9	10.6	11.9
NB4	1	30	0.25	1.53	0.38	0.63	2.55	1.7	2.9	1.9	3.2	4.6	5.1
NB4	2	60	0.09	3.52	0.33	1.10	11.73	1.5	5.0	1.7	5.6	6.5	7.3
NB4	3	90	0.07	3.88	0.28	0.19	2.58	1.3	0.8	1.4	0.9	2.1	2.4
NB4	4	120	0.09	47.09	4.46	0.85	8.97	20.1	3.8	22.6	4.3	23.9	26.9
NB4	5	150	0.06	111.71	6.34	0.95	16.76	28.5	4.3	32.0	4.8	32.8	36.8
NB5	1	30	0.20	9.86	1.98	1.43	7.12	8.9	6.4	10.0	7.2	15.3	17.2
NB5	2	60	0.10	21.93	2.16	0.66	6.67	9.7	3.0	10.9	3.3	12.7	14.3
NB5	3	90	0.07	28.77	2.06	0.82	11.51	9.2	3.7	10.4	4.2	12.9	14.5
NB5	4	120	0.08	19.21	1.51	1.13	14.41	6.8	5.1	7.6	5.7	11.9	13.3

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
NB5	5	150	0.08	31.31	2.45	0.96	12.25	11.0	4.3	12.4	4.9	15.4	17.3
NB7	1	30	0.08	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB7	2	60	0.09	0.00	0.00	0.29	3.22	0.0	1.3	0.0	1.5	1.3	1.5
NB7	3	90	0.08	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB7	4	120	0.11	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB7	5	150	0.13	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB8	1	30	0.08	0.00	0.00	0.50	6.00	0.0	2.3	0.0	2.5	2.3	2.5
NB8	2	60	0.13	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB8	3	90	0.12	0.00	0.00	0.50	4.15	0.0	2.3	0.0	2.5	2.3	2.5
NB8	4	120	0.09	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
NB8	5	150	0.05	0.00	0.00	0.63	13.70	0.0	2.8	0.0	3.2	2.8	3.2
NC2	1	30	0.10	9.93	1.04	3.60	34.31	4.7	16.2	5.3	18.2	20.9	23.5
NC2	2	60	0.11	13.79	1.56	1.25	11.03	7.0	5.6	7.9	6.3	12.7	14.2
NC2	3	90	0.09	16.16	1.53	1.24	13.13	6.9	5.6	7.7	6.3	12.5	14.0
NC2	4	120	0.10	42.07	4.21	5.05	50.48	18.9	22.7	21.3	25.5	41.6	46.8
NC2	5	150	0.13	179.61	22.84	1.46	11.51	102.8	6.6	115.5	7.4	109.4	122.9
NC4	1	30	0.23	26.27	6.16	1.45	6.18	27.7	6.5	31.2	7.3	34.3	38.5
NC4	2	60	0.22	33.57	7.40	1.23	5.59	33.3	5.5	37.4	6.2	38.8	43.6
NC4	3	90	0.15	39.11	5.89	1.53	10.14	26.5	6.9	29.8	7.7	33.4	37.5
NC5	1	30	0.19	30.26	5.69	1.71	9.08	25.6	7.7	28.8	8.6	33.3	37.4
NC5	2	60	0.12	37.44	4.53	1.36	11.23	20.4	6.1	22.9	6.9	26.5	29.8
NC5	3	90	0.08	48.08	3.98	0.97	11.73	17.9	4.4	20.1	4.9	22.3	25.1
NC5	4	120	0.08	42.95	3.64	1.27	15.03	16.4	5.7	18.4	6.4	22.1	24.8
NC5	5	150	0.07	67.15	4.94	0.62	8.39	22.2	2.8	25.0	3.1	25.0	28.1
NC7	1	30	0.14	1.63	0.23	0.00	0.00	1.0	0.0	1.1	0.0	1.0	1.1
NC7	2	60	0.14	0.00	0.00	0.33	2.30	0.0	1.5	0.0	1.7	1.5	1.7
NC7	3	90	0.06	0.00	0.00	0.29	4.58	0.0	1.3	0.0	1.5	1.3	1.5
NC7	4	120	0.09	0.00	0.00	0.66	7.04	0.0	3.0	0.0	3.3	3.0	3.3
NC7	5	150	0.07	0.00	0.00	0.45	6.63	0.0	2.0	0.0	2.3	2.0	2.3
P1	1	30	0.73	0.00	0.00	15.98	21.81	0.0	71.9	0.0	80.8	71.9	80.8
P1	2	60	0.74	0.00	0.00	5.23	7.07	0.0	23.5	0.0	26.5	23.5	26.5
P1	2	60	0.49	0.00	0.00	4.39	8.89	0.0	210.8	0.0	236.9	210.8	236.9
P1		0	2.73	0.00	0.00	46.85	17.15	0.0	19.8	0.0	22.2	19.8	22.2
PN2	1	30	0.14	0.00	0.00	1.60	11.27	0.0	7.2	0.0	8.1	7.2	8.1
PN2	2	60	0.23	0.00	0.00	1.73	7.67	0.0	7.0	0.0	7.9	7.0	7.9
PN2	2	60	0.20	0.00	0.00	1.56	7.73	0.0	7.8	0.0	8.8	7.8	8.8
PN2	3	90	0.22	0.00	0.00	3.12	13.97	0.0	8.0	0.0	9.0	8.0	9.0
PN2	3	90	0.17	0.00	0.00	1.79	10.29	0.0	14.0	0.0	15.8	14.0	15.8
PN2	4	120	0.21	0.00	0.00	1.65	7.96	0.0	7.4	0.0	8.3	7.4	8.3
PN3	1	30	0.21	0.00	0.00	3.13	15.01	0.0	14.1	0.0	15.8	14.1	15.8

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
PN3	2	60	0.18	0.00	0.00	3.48	19.23	0.0	15.7	0.0	17.6	15.7	17.6
PN3	3	90	0.19	0.00	0.00	2.09	10.77	0.0	4.1	0.0	4.6	4.1	4.6
PN3	3	90	0.19	0.00	0.00	0.92	4.84	0.0	9.4	0.0	10.6	9.4	10.6
PN3	4	120	0.23	0.00	0.00	1.37	5.95	0.0	3.3	0.0	3.8	3.3	3.8
PN3	4	120	0.20	0.00	0.00	0.74	3.68	0.0	6.2	0.0	6.9	6.2	6.9
PN4	1	30	0.14	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
PN4	2	60	0.17	0.00	0.00	0.83	4.86	0.0	3.7	0.0	4.2	3.7	4.2
PN4	3	90	0.16	0.00	0.00	1.17	7.14	0.0	5.2	0.0	5.9	5.2	5.9
PN5	1	30	0.19	15.44	2.92	2.49	13.15	13.1	11.2	14.8	12.6	24.3	27.3
PN5	2	60	0.15	14.69	2.24	0.51	3.34	10.1	2.3	11.3	2.6	12.4	13.9
PN5	3	90	0.24	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
PN5	3	90	0.22	0.00	0.00	3.10	14.29	0.0	13.9	0.0	15.7	13.9	15.7
PN5	4	120	0.21	0.00	0.00	2.89	13.72	0.0	13.0	0.0	14.6	13.0	14.6
PN5	4	120	0.20	0.00	0.00	3.00	14.86	0.0	13.5	0.0	15.2	13.5	15.2
PN6	1	30	0.07	2.58	0.19	0.67	9.04	0.9	3.0	1.0	3.4	3.9	4.4
PN6	2	60	0.10	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
PN6	3	90	1.03	0.21	0.21	6.59	6.41	1.0	29.7	1.1	33.3	30.6	34.4
PN7	1	30	0.09	65.82	6.15	1.33	14.26	27.7	6.0	31.1	6.7	33.7	37.9
PN7	2	60	0.18	0.00	0.00	1.75	9.52	0.0	7.9	0.0	8.8	7.9	8.8
PN7	3	90	0.27	0.45	0.12	1.92	7.18	0.5	8.6	0.6	9.7	9.2	10.3
PN7	4	120	0.18	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
PN8	1	30	0.13	0.75	0.09	1.89	14.91	0.4	8.5	0.5	9.5	8.9	10.0
PN8	2	60	0.09	0.00	0.00	0.28	3.03	0.0	1.3	0.0	1.4	1.3	1.4
PN8	3	90	0.17	0.00	0.00	1.40	8.34	0.0	6.3	0.0	7.1	6.3	7.1
PS2	1	30	2.77	3.34	9.25	34.42	12.44	41.6	154.9	46.8	174.0	196.5	220.8
PS2	2	60	1.07	0.20	0.21	15.50	14.45	1.0	69.8	1.1	78.4	70.7	79.4
PS2	3	90	3.23	0.00	0.00	20.04	6.20	0.0	90.2	0.0	101.3	90.2	101.3
PS2	4	120	5.00	0.00	0.00	2.88	0.58	0.0	13.0	0.0	14.6	13.0	14.6
PS2A	1	30	0.41	3.83	1.57	6.15	14.96	7.1	27.7	8.0	31.1	34.7	39.0
PS2A	2	60	0.46	11.76	5.45	10.91	23.51	24.5	49.1	27.6	55.2	73.6	82.7
PS2A	3	90	3.31	0.00	0.00	64.02	19.36	0.0	288.1	0.0	323.7	288.1	323.7
PS3	1	30	0.44	3.78	1.65	6.18	14.17	0.0	168.5	0.0	189.3	168.5	189.3
PS3	1	30	3.59	0.00	0.00	37.45	10.44	7.4	27.8	8.3	31.2	35.2	39.6
PS3	2	60	5.42	0.00	0.00	50.10	9.25	0.0	225.5	0.0	253.3	225.5	253.3
PS4	1	30	0.23	6.63	1.51	1.86	8.16	6.8	8.4	7.6	9.4	15.2	17.0
PS4	2	60	0.40	0.00	0.00	1.90	4.71	0.0	8.6	0.0	9.6	8.6	9.6
PS4	4	120	4.43	0.13	0.57	60.47	13.66	2.5	272.1	2.9	305.7	274.6	308.6
PS5	1	30	0.14	17.89	2.59	3.13	21.61	11.7	14.1	13.1	15.8	25.8	29.0
PS5	2	60	0.14	1.66	0.23	1.13	8.30	1.0	5.1	1.1	5.7	6.1	6.9
PS5	3	90	0.45	0.94	0.43	0.00	0.00	1.9	0.0	2.2	0.0	1.9	2.2

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
PS5	4	120	0.39	0.00	0.00	0.26	0.66	0.0	1.2	0.0	1.3	1.2	1.3
PS5	5	150	0.15	0.69	0.10	1.43	9.73	0.5	6.4	0.5	7.2	6.9	7.8
PS5	6	180	0.24	0.00	0.00	4.86	20.51	0.0	21.9	0.0	24.6	21.9	24.6
PS5	7	210	0.12	0.00	0.00	0.41	3.27	0.0	1.7	0.0	1.9	1.7	1.9
PS5	7	210	0.11	0.00	0.00	0.37	3.43	0.0	1.8	0.0	2.1	1.8	2.1
PS5.5	1	30	0.19	0.00	0.00	1.08	5.58	0.0	4.8	0.0	5.4	4.8	5.4
PS5.5	2	60	0.17	0.00	0.00	0.22	1.32	0.0	1.0	0.0	1.1	1.0	1.1
PS5.5	3	90	0.17	0.00	0.00	1.29	7.43	0.0	5.8	0.0	6.5	5.8	6.5
PS5.5	4	120	0.11	0.00	0.00	0.50	4.68	0.0	2.2	0.0	2.5	2.2	2.5
PS5.5	5	150	0.15	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
PS5.5	6	180	0.05	0.00	0.00	0.28	6.03	0.0	1.3	0.0	1.4	1.3	1.4
PS5.5	7	210	0.05	0.00	0.00	2.03	39.89	0.0	9.1	0.0	10.2	9.1	10.2
PS5.5	8	240	0.09	0.00	0.00	0.53	5.61	0.0	2.4	0.0	2.7	2.4	2.7
PS5D	1	30	0.13	0.00	0.00	1.02	7.79	0.0	4.6	0.0	5.2	4.6	5.2
PS5D	2	60	0.09	0.00	0.00	0.77	8.24	0.0	3.5	0.0	3.9	3.5	3.9
PS5D	3	90	0.07	1.40	0.10	0.00	0.00	0.4	0.0	0.5	0.0	0.4	0.5
PS5D	4	120	0.09	0.00	0.00	3.11	35.44	0.0	14.0	0.0	15.7	14.0	15.7
PS5D	5	150	0.07	1.40	0.10	0.42	5.60	0.5	1.9	0.5	2.1	2.3	2.6
PS5D	10	300	0.07	6.81	0.49	0.29	4.08	2.2	1.3	2.5	1.5	3.5	3.9
PS6	1	30	0.32	1.21	0.38	0.00	0.00	1.7	0.0	1.9	0.0	1.7	1.9
PS6	2	60	1.63	0.00	0.00	24.32	14.93	0.0	109.4	0.0	123.0	109.4	123.0
PS6A	1	30	0.25	1.31	0.33	5.32	20.99	1.5	23.9	1.7	26.9	25.4	28.6
PS6A	2	60	0.76	0.00	0.00	12.22	16.09	0.0	55.0	0.0	61.8	55.0	61.8
PS7	1	30	0.21	9.25	1.91	1.79	8.67	8.6	8.1	9.7	9.1	16.7	18.7
PS7	2	60	0.21	1.72	0.37	0.61	2.86	1.7	2.8	1.9	3.1	4.4	4.9
PS7	3	90	0.81	0.00	0.00	7.87	9.71	0.0	35.4	0.0	39.8	35.4	39.8
PS7A	1	30	0.20	13.63	2.67	1.34	6.82	12.0	6.0	13.5	6.8	18.1	20.3
PS7D	1	30	0.13	3.21	0.43	0.54	4.02	1.9	2.4	2.2	2.7	4.3	4.9
PS7D	2	60	0.07	2.65	0.20	0.39	5.30	0.9	1.8	1.0	2.0	2.7	3.0
PS7D	3	90	0.10	2.97	0.29	0.68	6.93	1.3	3.1	1.5	3.4	4.4	4.9
PS7D	4	120	0.08	3.88	0.33	0.66	7.75	1.5	3.0	1.7	3.3	4.4	5.0
PS7D	5	150	0.07	4.08	0.29	0.00	0.00	1.3	0.0	1.5	0.0	1.3	1.5
PS8	1	30	0.16	5.88	0.93	3.01	19.10	4.2	13.5	4.7	15.2	17.7	19.9
PS8	2	60	0.16	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA2	1	30	0.17	12.56	2.12	1.01	5.98	9.5	4.5	10.7	5.1	14.1	15.8
SA2	2	60	0.21	111.10	23.52	2.10	9.94	105.8	9.5	118.9	10.6	115.3	129.5
SA2	3	90	0.30	36.27	10.99	1.29	4.27	49.5	5.8	55.6	6.5	55.3	62.1
SA2	4	120	0.29	10.09	2.96	3.20	10.90	13.3	14.4	15.0	16.2	27.7	31.1
SA3	1	30	0.15	7.35	1.13	1.94	12.69	5.1	8.7	5.7	9.8	13.8	15.5
SA3	2	60	0.10	9.66	0.96	2.46	24.70	4.3	11.1	4.9	12.5	15.4	17.3

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
SA3	3	90	0.18	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA3	3	90	0.10	19.81	1.96	0.78	7.92	8.8	3.5	9.9	4.0	12.4	13.9
SA3	4	120	0.11	127.32	13.91	1.71	15.70	62.6	7.7	70.3	8.7	70.3	79.0
SA3	5	150	0.16	88.56	14.59	2.94	17.86	65.7	13.2	73.8	14.9	78.9	88.6
SA4	1	30	0.14	7.14	0.99	0.00	0.00	4.5	0.0	5.0	0.0	4.5	5.0
SA4	2	60	0.22	65.15	14.46	0.00	0.00	65.1	0.0	73.1	0.0	65.1	73.1
SA4	3	90	0.23	184.01	42.05	1.38	6.02	189.2	6.2	212.6	7.0	195.4	219.5
SA4	4	120	0.17	11.66	1.95	0.80	4.80	8.8	3.6	9.9	4.1	12.4	13.9
SA4	5	150	0.13	8.30	1.10	0.00	0.00	5.0	0.0	5.6	0.0	5.0	5.6
SA5	1	30	0.15	0.00	0.00	0.61	4.01	0.0	2.8	0.0	3.1	2.8	3.1
SA5	2	60	0.18	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA5	4	120	0.09	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA5	5	150	0.11	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA6	1	30	0.22	2.50	0.55	1.65	7.50	2.5	7.4	2.8	8.3	9.9	11.1
SA6	2	60	0.18	2.60	0.47	0.71	3.91	2.1	3.2	2.4	3.6	5.3	6.0
SA6	2	60	0.20	7.87	1.58	0.36	1.82	7.1	1.6	8.0	1.8	8.7	9.8
SA6	3	90	0.18	1.18	0.22	0.00	0.00	1.0	0.0	1.1	0.0	1.0	1.1
SA6	4	120	0.10	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA6	5	150	0.07	2.52	0.19	0.19	2.52	0.8	0.8	0.9	0.9	1.7	1.9
SA7	1	30	0.16	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA7	2	60	0.11	3.61	0.38	0.00	0.00	1.7	0.0	1.9	0.0	1.7	1.9
SA7	3	90	0.09	4.48	0.42	0.00	0.00	1.9	0.0	2.1	0.0	1.9	2.1
SA7	4	120	0.11	4.60	0.52	0.00	0.00	2.4	0.0	2.6	0.0	2.4	2.6
SA7	5	150	0.09	3.22	0.28	0.18	2.15	1.2	0.8	1.4	0.9	2.1	2.3
SA8	1	30	0.14	3.43	0.49	0.68	4.80	2.2	3.1	2.5	3.4	5.2	5.9
SA8	2	60	0.17	3.34	0.58	0.00	0.00	2.6	0.0	2.9	0.0	2.6	2.9
SA8	3	90	0.09	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SA8	4	120	0.10	7.21	0.73	0.00	0.00	3.3	0.0	3.7	0.0	3.3	3.7
SA8	5	150	0.06	31.21	1.74	0.00	0.00	7.8	0.0	8.8	0.0	7.8	8.8
SB2	1	30	0.14	22.04	3.13	3.13	22.04	14.1	14.1	15.8	15.8	28.1	31.6
SB2	2	60	0.08	27.05	2.28	0.00	0.00	10.2	0.0	11.5	0.0	10.2	11.5
SB2	3	90	0.12	53.07	6.14	0.85	7.35	27.6	3.8	31.0	4.3	31.4	35.3
SB2	4	120	0.09	56.56	5.09	4.31	47.95	22.9	19.4	25.7	21.8	42.3	47.5
SB2	5	150	0.07	58.14	3.87	1.89	28.43	17.4	8.5	19.6	9.6	25.9	29.1
SB3	1	30	0.18	28.45	5.05	2.15	12.10	22.7	9.7	25.5	10.9	32.4	36.4
SB3	2	60	0.10	51.48	5.27	0.86	8.42	23.7	3.9	26.7	4.4	27.6	31.0
SB3	3	90	0.06	91.58	5.25	1.03	17.96	23.6	4.6	26.6	5.2	28.3	31.8
SB3	4	120	0.08	112.99	8.97	0.86	10.89	40.4	3.9	45.4	4.4	44.3	49.7
SB3	5	150	0.07	138.49	9.81	3.67	51.76	44.2	16.5	49.6	18.5	60.7	68.2
SB4	1	30	0.21	83.44	17.84	0.00	0.00	80.3	0.0	90.2	0.0	80.3	90.2

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
SB4	2	60	0.23	118.71	26.94	0.21	0.95	121.2	1.0	136.2	1.1	122.2	137.3
SB4	3	90	0.14	90.01	12.63	0.56	4.02	56.8	2.5	63.9	2.9	59.4	66.7
SB4	4	120	0.13	58.67	7.41	0.20	1.61	33.3	0.9	37.5	1.0	34.2	38.5
SB4	5	150	0.14	53.81	7.26	0.43	3.17	32.7	1.9	36.7	2.2	34.6	38.9
SB5	1	30	0.15	1.45	0.22	0.77	5.07	1.0	3.5	1.1	3.9	4.5	5.0
SB5	2	60	0.17	0.00	0.00	0.22	1.30	0.0	1.0	0.0	1.1	1.0	1.1
SB5	3	90	0.12	0.00	0.00	0.31	2.57	0.0	1.4	0.0	1.6	1.4	1.6
SB5	4	120	0.15	8.45	1.27	0.64	4.23	5.7	2.9	6.4	3.2	8.6	9.6
SB5	5	150	0.12	7.98	0.93	5.66	48.80	4.2	25.5	4.7	28.6	29.7	33.3
SB6	1	30	0.13	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SB6	2	60	0.11	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SB6	3	90	0.09	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SB6	4	120	0.05	0.00	0.00	0.18	3.47	0.0	0.8	0.0	0.9	0.8	0.9
SB6	5	150	0.05	0.00	0.00	0.10	1.93	0.0	0.5	0.0	0.5	0.5	0.5
SB7	1	30	0.15	0.00	0.00	0.53	3.43	0.0	2.4	0.0	2.7	2.4	2.7
SB7	2	60	0.13	0.00	0.00	0.45	3.55	0.0	2.0	0.0	2.3	2.0	2.3
SB7	3	90	0.08	3.78	0.29	0.00	0.00	1.3	0.0	1.5	0.0	1.3	1.5
SB7	4	120	0.07	11.36	0.75	0.00	0.00	3.4	0.0	3.8	0.0	3.4	3.8
SB7	5	150	0.07	8.17	0.60	0.00	0.00	2.7	0.0	3.0	0.0	2.7	3.0
SB8	1	30	0.17	15.38	2.58	0.40	2.37	11.6	1.8	13.0	2.0	13.4	15.0
SB8	2	60	0.19	23.21	4.37	0.00	0.00	19.7	0.0	22.1	0.0	19.7	22.1
SB8	3	90	0.19	3.25	0.62	0.00	0.00	2.8	0.0	3.2	0.0	2.8	3.2
SB8	4	120	0.08	55.82	4.19	0.00	0.00	18.9	0.0	21.2	0.0	18.9	21.2
SB8	5	150	0.11	9.90	1.04	0.00	0.00	4.7	0.0	5.3	0.0	4.7	5.3
SC2	1	30	0.21	336.84	69.91	0.00	0.00	314.6	0.0	353.5	0.0	314.6	353.5
SC2	2	60	0.21	393.51	82.89	5.05	23.97	373.0	22.7	419.1	25.5	395.8	444.7
SC2	3	90	0.14	249.69	35.13	1.05	7.44	158.1	4.7	177.6	5.3	162.8	182.9
SC2	4	120	0.06	309.78	19.91	6.06	94.35	89.6	27.3	100.6	30.7	116.9	131.3
SC2	5	150	0.12	231.56	27.85	2.13	17.74	125.3	9.6	140.8	10.8	134.9	151.6
SC3	1	30	0.19	8.06	1.56	1.20	6.20	7.0	5.4	7.9	6.1	12.4	14.0
SC3	2	60	0.13	26.11	3.30	0.60	4.75	14.9	2.7	16.7	3.0	17.6	19.7
SC3	3	90	0.08	32.84	2.73	0.59	7.04	12.3	2.6	13.8	3.0	14.9	16.8
SC3	4	120	0.07	25.82	1.85	1.67	23.36	8.3	7.5	9.3	8.5	15.8	17.8
SC3	5	150	0.09	50.46	4.47	1.75	19.75	20.1	7.9	22.6	8.8	28.0	31.5
SC4	1	30	0.12	120.08	14.25	1.61	13.54	64.1	7.2	72.0	8.1	71.3	80.2
SC4	2	60	0.08	42.02	3.56	0.00	0.00	16.0	0.0	18.0	0.0	16.0	18.0
SC4	3	90	0.08	96.78	7.63	0.63	7.95	34.3	2.8	38.6	3.2	37.2	41.8
SC4	4	120	0.07	96.52	6.54	0.00	0.00	29.4	0.0	33.1	0.0	29.4	33.1
SC4	5	150	0.10	82.20	8.57	0.72	6.93	38.6	3.3	43.3	3.7	41.8	47.0
SC5	1	30	0.16	5.08	0.83	0.83	5.08	3.7	3.7	4.2	4.2	7.5	8.4

Table 11: Data from analysis of soil samples collected 12/1/96 – 1/15/97 (continued).

Site ID	Depth (ft)	Depth(cm)	Water content of soil (mass H_2O/mass dry soil)	Concentration of NO_3^- in water (ppm)	Concentration of NO_3^- (expressed in ppm dry soil)	Concentration of NH_4^+ (expressed in ppm dry soil)	Concentration of NH_4^+ in water (ppm)	NO_3^- (Kg/ha)	NH_4^+ (Kg/ha)	NO_3^- (lbs/ac)	NH_4^+ (lbs/ac)	Total residual N (Kg/ha)	Total residual N (lbs/acre)
SC5	2	60	0.19	2.54	0.47	0.36	1.91	2.1	1.6	2.4	1.8	3.7	4.2
SC5	3	90	0.15	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.0	0.0
SC5	4	120	0.12	1.74	0.22	0.00	0.00	1.0	0.0	1.1	0.0	1.0	1.1
SC5	5	150	0.09	7.21	0.68	0.00	0.00	3.1	0.0	3.4	0.0	3.1	3.4
SC6	1	30	0.22	5.25	1.17	0.23	1.05	5.3	1.1	5.9	1.2	6.3	7.1
SC6	3	90	0.18	0.00	0.00	0.75	4.29	0.0	3.4	0.0	3.8	3.4	3.8
SC6	5	150	0.10	12.63	1.28	0.00	0.00	5.8	0.0	6.5	0.0	5.8	6.5
SC7	1	30	0.17	13.90	2.35	0.71	4.17	10.6	3.2	11.9	3.6	13.8	15.5
SC7	2	60	0.23	15.01	3.49	0.47	2.00	15.7	2.1	17.7	2.4	17.8	20.0
SC7	3	90	0.17	35.16	6.13	0.57	3.26	27.6	2.6	31.0	2.9	30.2	33.9
SC7	4	120	0.14	33.54	4.64	0.00	0.00	20.9	0.0	23.4	0.0	20.9	23.4
SC7	5	150	0.16	31.54	5.07	0.00	0.00	22.8	0.0	25.7	0.0	22.8	25.7
SC8	1	30	0.17	1.25	0.21	0.83	5.02	0.9	3.7	1.1	4.2	4.7	5.3
SC8	2	60	0.15	5.22	0.78	0.67	4.47	3.5	3.0	4.0	3.4	6.5	7.4
SC8	3	90	0.07	2.88	0.20	0.00	0.00	0.9	0.0	1.0	0.0	0.9	1.0
SC8	4	120	0.08	47.09	3.96	0.00	0.00	17.8	0.0	20.0	0.0	17.8	20.0
SC8	5	150	0.05	8.98	0.47	0.09	1.80	2.1	0.4	2.4	0.5	2.6	2.9

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