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A Study of Ground-Water Quality in a Priority Agricultural and Livestock Watershed, Cass County, Michigan

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A STUDY OF GROUND-WATER QUALITY IN A PRIORITY AGRICULTURAL AND LIVESTOCK WATERSHED, CASS COUNTY, MICHIGAN

by

Matthew Alan Stuk

A Thesis
Submitted to the
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in partial fulfillment of the
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Department of Geology

Western Michigan University
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A STUDY OF GROUND-WATER QUALITY IN A PRIORITY AGRICULTURAL AND LIVESTOCK WATERSHED, CASS COUNTY, MICHIGAN

Matthew Alan Stuk, M.S.

Western Michigan University, 1992

A study of ground-water contamination in a shallow, sandy, glacial drift aquifer was performed in a watershed dominated by swine feedlots and crop fields in Cass County, Michigan. Monitoring wells were installed and sampled to study the flow pattern, chemistry, and contamination of ground water.

Results of chemical analyses show contamination from fertilizers and other soil-applied chemicals as well as the infiltration of breakdown products from pig waste. Shallow wells in impacted areas show potassium and nitrate from the breakdown of fertilizers, calcium from field application of lime, and additional nitrate from pig waste. Elevated calcium, potassium, and nitrate concentrations were observed in shallow wells and decreased with depth. Contamination effects were generally confined to upper zones of the aquifer because of the local ground-water flow pattern and the stratigraphy of the glacial drift.

ACKNOWLEDGMENTS

I would like to thank the people who made the completion of this project possible. I owe much of the credit to my thesis committee, Dr. Thomas Straw, Dr. Alan Kehew, and Dr. Richard Passero, for guidance on my thesis preparation as well as coordination of drilling and sampling projects. I also thank the various students who assissted in drilling, sampling, and surveying. Most of all, I would like to thank my parents for their support throughout my seemingly endless years of education.

Matthew Alan Stuk

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INTRODUCTION

The contamination of ground water from agricultural practices and livestock holdings has become a serious problem in southwestern Michigan (Kittleson, 1987). The relatively shallow aquifers and highly permeable, sandy soils combine to make the ground water in the region very vulnerable to degradation from surface activities. Reliance of the rural population on private wells for water has caused concern especially because of the lack of water quality regulation for private well supplies. High levels of nitrate (NO_3^-) in rural ground water have been known for decades to be a direct result of agricultural and livestock practices (Hubbard, 1989). The consequence of prolonged exposure to nitrates is not well known, although many cases of methemoglobinemia (blue baby syndrome) have been reported and linked to high nitrate drinking water (Bouwer, 1987). Methemoglobinemia is a result of the internal reduction of nitrate to nitrite. Also, coupling of nitrite with amine groups may form nitrosamines which are known carcinogens (Bouwer, 1990).

Background ground-water chemistry is dominated by calcium, bicarbonate, magnesium, and sulfate, which is typical of a sandy aquifer. Hydrochemistry changes sharply from background to areas of agricultural and livestock impact. Previous studies of the Donnell lake watershed in Cass County, Michigan, showed high levels of nitrate in the shallow ground-water aquifer often exceeding the maximum contaminant level (MCL) of 10 mg/L NO_3-N (Alexander, 1991). The contamination of ground water has previously been attributed to leaching of fertilizers from croplands and runoff from swine operations (National Research Council, 1978).

Monitoring wells were installed and sampled to better define the magnitude of ground-water contamination in this area. Results from the analyses support the previous studies showing a relationship between agriculture and livestock operations and ground-water degradation.

SITE DESCRIPTION

Location

The study site is located in Cass County, Michigan near Vandalia (Fig. 1). The site occupies sections 25, 26, 35, and 36 of Penn Township and sections 30 and 31 of Newberg Township (Fig. 2).

Topography

The topography of the area is defined by gently rolling hills with the highest elevation in the northeastern part of the area sloping towards the southwest in the direction of the watershed outlet (Fig. 3).

Soils

The soils in the area include soil series of the Kalamazoo-Oshtemo association. These are defined by the Soil Survey as hilly, well-drained, sandy and loamy soils. In areas of high swine density soils are often compacted. This results in decreased infiltration rates and ponding in lower areas.

Landuse

Landuse in the Donnell Lake watershed is shown in

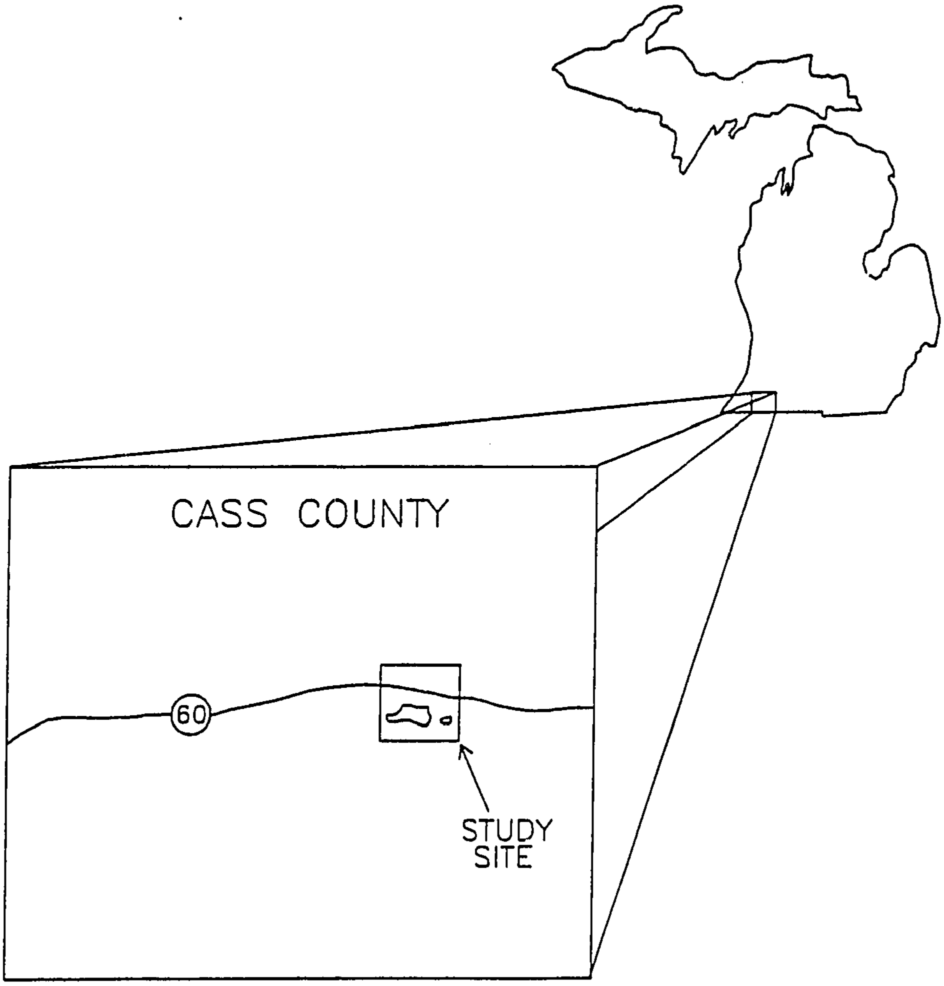


Figure 1. Location of Study Site in Cass County, Michigan.

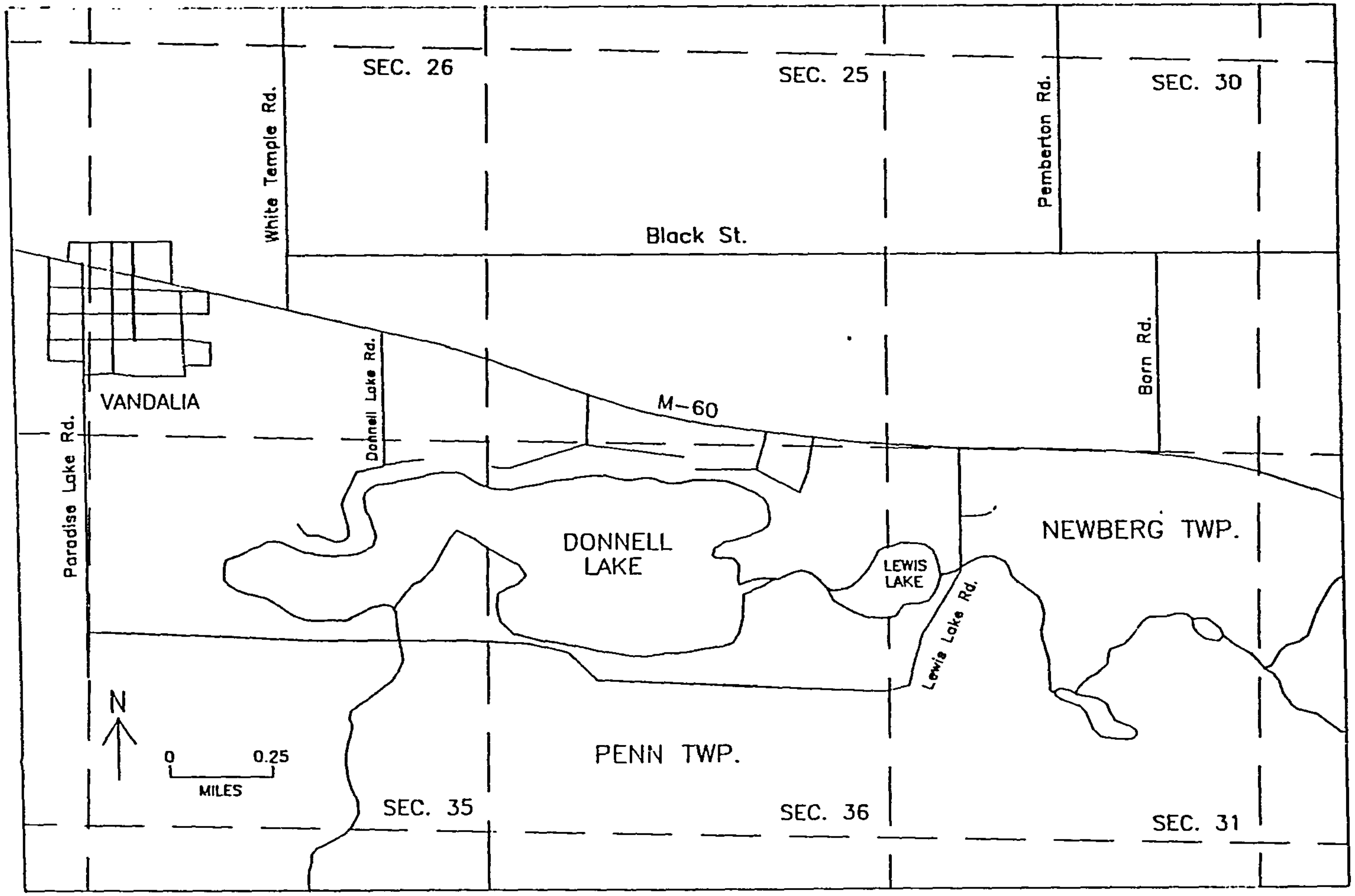


Figure 2. Donnell Lake Study Site, Cass County, Michigan.

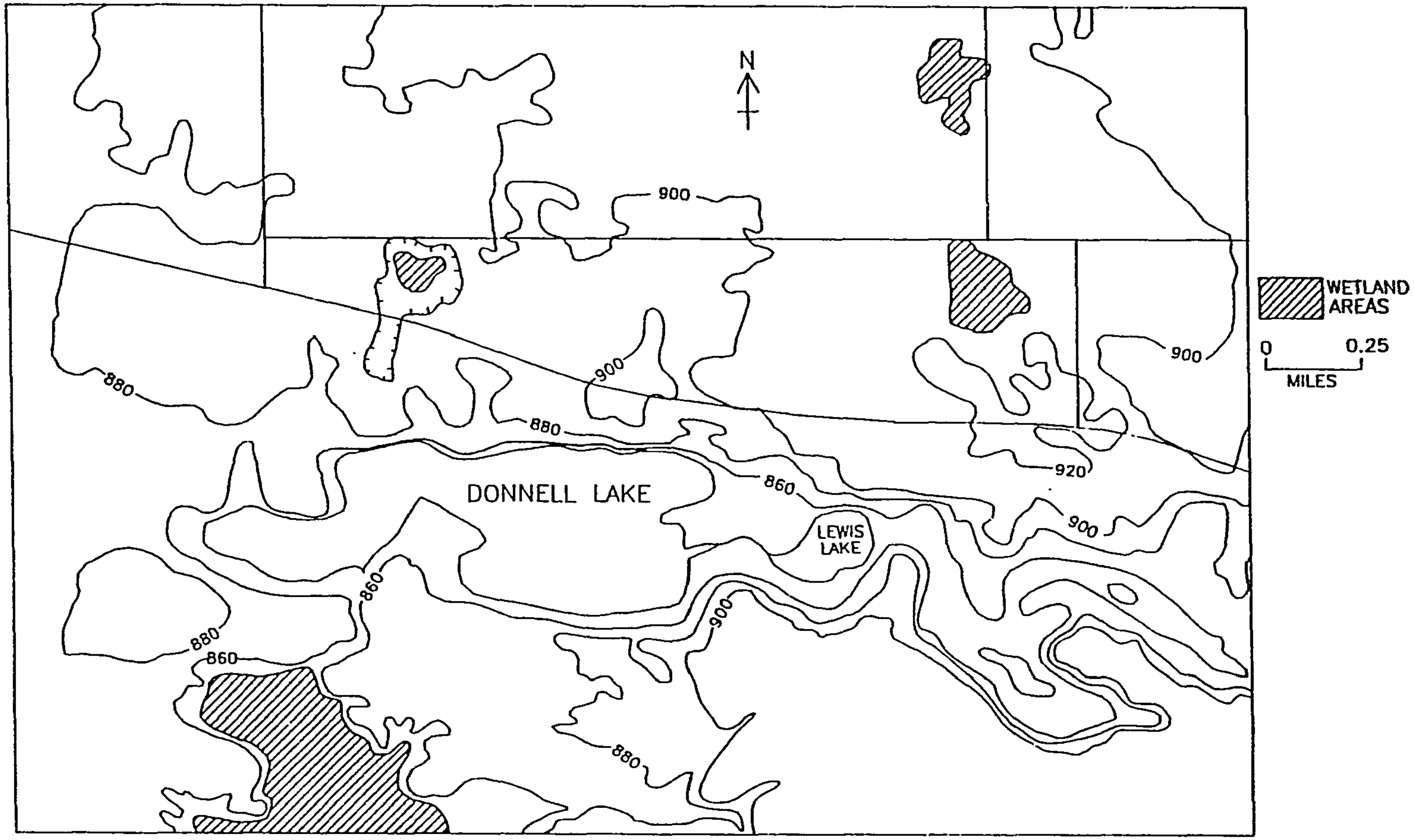


Figure 3. Donnell Lake Area Topography.

Figure 4. Croplands are primarily corn and soybeans, and livestock facilities are mainly open pasture hog lots except for a semi-confinement hog facility located on the west side of Born Road.

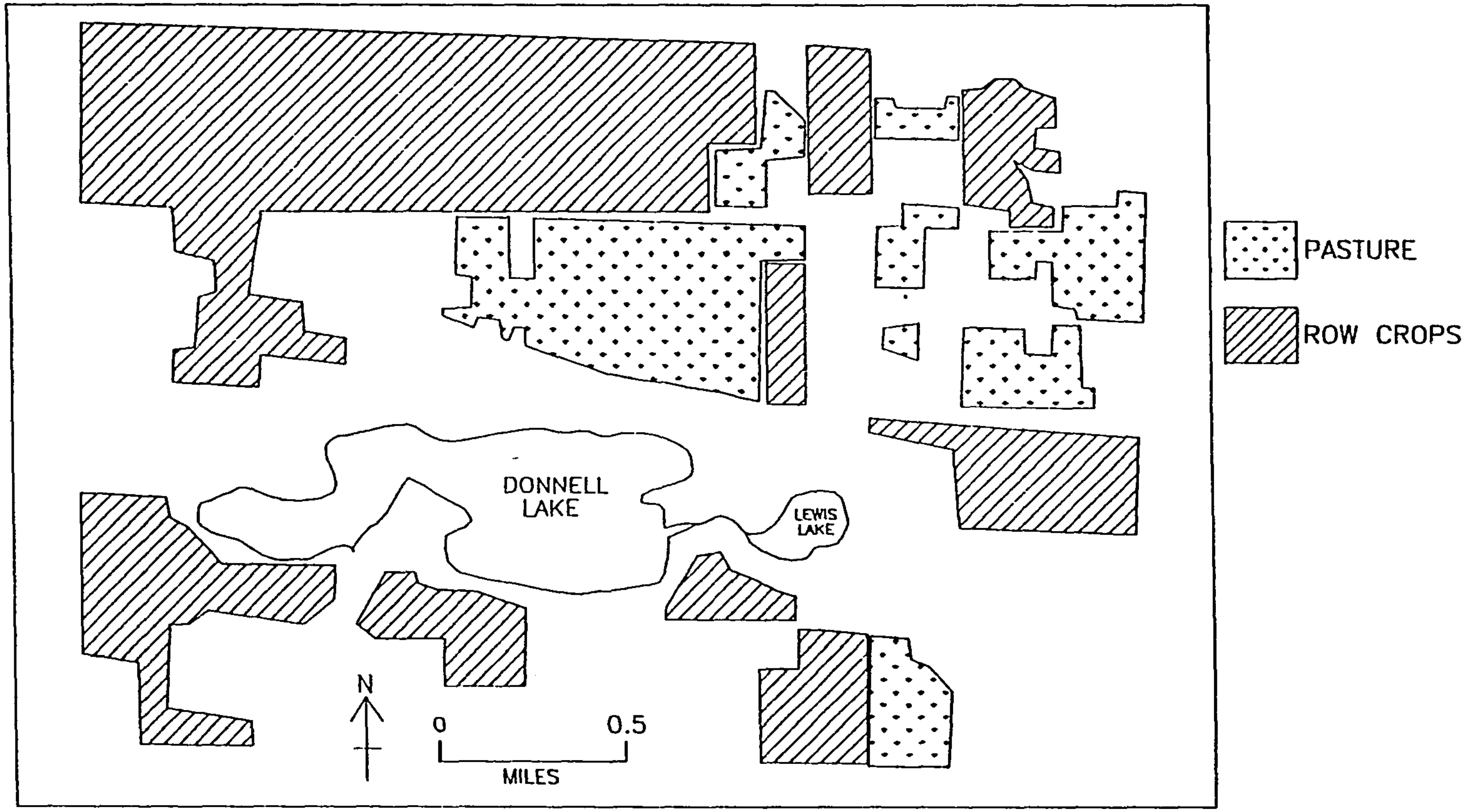


Figure 4. Donnell Lake Area Landuse.

METHODOLOGY

This study was an extension of ground-water testing done in and around the Donnell Lake area by Michigan State University (MSU). Financial support from the U.S. Environmental Protection Agency through Michigan State University was used for well drilling and water chemistry analyses. An additional grant from the Geological Society of America was used for well drilling.

Twenty-three monitoring wells were installed in 11 nests to provide an areal and vertical representation of ground-water flow systems and water chemistry within the shallow aquifer system (Fig. 5 and Table 1). The well nests also allow interpretation of the aquifer flow regime. The nests were installed in three north-south trending alignments roughly perpendicular to potentiometric contours. This was done to determine water chemistry changes with respect to well location and flow path. Residential wells near well nest locations 2, 3, 4, 6, 7, 8, 9, and 10 were included to give better vertical chemical representation at the sampling locations. This gave most of the nests a shallow, intermediate, and deep well. Well depths vary from 1 to 6 feet below the water table for shallow wells, 17 to 53 feet below the water table for intermediate wells, and 49 to 69 feet below the water table for deep

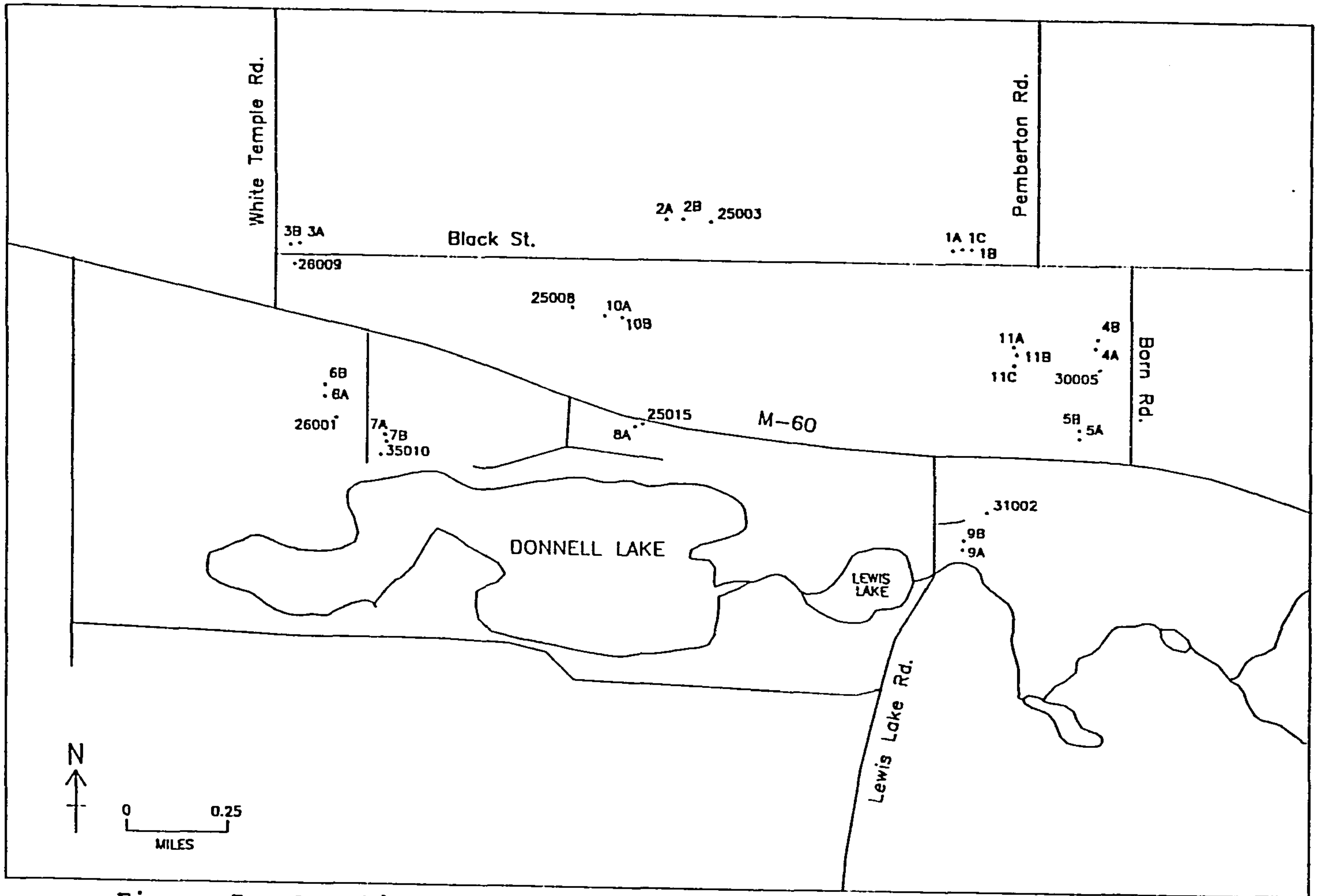


Figure 5. Location of WMU Monitoring Wells and Residential Wells.

Table 1

WMU Monitoring Well Installation Data

Well I.D.	Depth* (feet)	Screen Int. (feet)	Casing	Drilling Method	Sampling Method
1A	71	66-71	PVC	MR	SS-10'
1B	38	33-38	PVC	HSA	Auger
1C	13	8-13	PVC	HSA	Auger
2A	28	23-28	PVC	HSA	Auger
2B	88	73-78	PVC	MR	SS (>40')
3A	28	23-28	PVC	HSA	Auger
3B	80	72-77	PVC	MR	SS (>40')
4A	33	28-33	PVC	HSA	Auger
4B	44	39-44	PVC	MR	SS-5'
5A	43	38-43	PVC	HSA	Auger
5B	62.5	57.5-62.5	PVC	MR	SS
6A	73	68-73	PVC	MR	SS
6B	34	29-34	PVC	HSA	Auger
7A	93	88-93	PVC	MR	SS
7B	43	38-43	PVC	HSA	Auger
8A	53.5	48.5-53.5	PVC	HSA	Auger
9A	19	14-19	PVC	HSA	Auger
9B	42.5	37.5-42.5	PVC	HSA	SS (0-15') Auger (>15')
10A	74	71-74	GS	MR	SS
10B	21	16-21	PVC	HSA	Auger
11A	73	68-73	PVC	MR	SS
11B	19	16-19	GS	HSA	Auger
11C	38	33-38	PVC	HSA	Auger

* feet below ground level
PVC = Poly Vinyl Chloride (2" sch. 40)
GS = Galvanized Steel (2")
MR = Mud Rotary; HSA = Hollow Stem Auger
SS = Split Spoon (every 10' unless otherwise indicated)

wells. The monitoring wells will be sampled periodically for future studies to determine temporal changes in ground-water chemistry.

The monitoring and residential wells were sampled between 3/31/92 and 4/8/92. The wells were purged with a QED Purge Miser pump to remove three casing volumes of water. A Johnson-Keck SP-84 sampling pump was then lowered to slightly above the well screen and run to sufficiently purge the pump line and rinse the sampling bottles. Low-capacity in-line 0.45 micrometer filters were attached to the output of the Johnson-Keck pump and changed between each sample. Separate bottled samples for laboratory analysis were taken for metals, non-metals, and ammonia. The samples for metals analysis were acidified with HNO_3 to prevent complexation, and the ammonia samples were treated with H_2SO_4 to prevent nitrification. The bottles were chilled and returned to the Water Quality Lab at Western Michigan University where they where then refrigerated until time of analysis. Partial analyses were performed by the Water Quality labs at WMU and also at the Michigan Department of Health. Department of Health analyses included screening for pesticides.

Laboratory Procedures

Procedures for analysis of chemical and physical ground-water parameters by the Water Quality Lab at WMU are as follows:

SiO_2 - SO_4 - NO_3

Silica, sulfate, and nitrate were analyzed using the Chemetrics colorimetric procedure. Chemetrics reagent ampoules were broken in a sample aliquot and allowed to mix. The ampoules were placed in a Chemetrics System 1000 photometer. Absorbance readings were converted into concentrations by Chemetrics calibration charts.

Alkalinity - Cl

Alkalinity and chloride were determined using Chemetrics titration kits. Sample aliquots were titrated with Chemetrics reagent ampoules. Concentrations were read directly off the graduated ampoules.

NH_3

One drop of $MnSO_4$ solution, 0.5 mL of hypochlorous acid, and 0.6 mL of phenate reagent was added to preserved ammonia samples. The sample absorbance was read in a Beckman DU-6 spectrophotometer.

SO_4

5 mL of conditioning reagent was added to sulfate samples. The sample absorbance was read in a Beckman DU-6.

Ca - Mg - Na - K - Fe - Mn

Metals were analyzed using a Leeman Series 1000 ICP.

pH - Temperature

An Orion SA 230 probe was used while the wells were being sampled to determine field pH and temperature.

Conductivity

Conductivity was determined in the field using a YSI 3000 Temperature-Level-Conductivity meter.

Dissolved Oxygen

Dissolved oxygen was analyzed using a YSI Model 57 probe. The probe was lowered below the Johnson-Keck pump to give a fresh ground-water sample reading. Chemetrics kits were used on four wells along with the YSI probe to test precision. The results of the two methods were within 5% of each other.

GEOLOGY

The bedrock underlying the Donnell Lake watershed is the Coldwater Shale of Mississippian age. Depth to bedrock ranges from 200 to 400 feet below ground surface (Western Michigan University, 1981).

The Donnell Lake watershed is located between the Sturgis and the outer Kalamazoo moraines. The surficial deposits are classified as sandy drift composed of alternating layers of sand, gravel, clay, and till. The sediments were deposited by glacial and glaciofluvial processes. The sand and gravel outwash deposits were deposited by the retreating glaciers of the Saginaw and Lake Michigan lobes during the late Wisconsinan advance. The till layers were deposited directly by glaciers as basal and disintegration tills during advance and disintegration of ice lobes. Clay layers were most likely deposited within proglacial or kettle lakes during glacial stagnation and disintegration. The hummocky topography is a result of stagnation and gradual down-melting of the glacier producing the series of kettle lakes within the drainage system (Leverett and Taylor, 1915).

Geologic cross sections and cross-section locations are shown in Figures 6-12. Cross sections were constructed from monitoring well gamma ray logs and split spoon samples

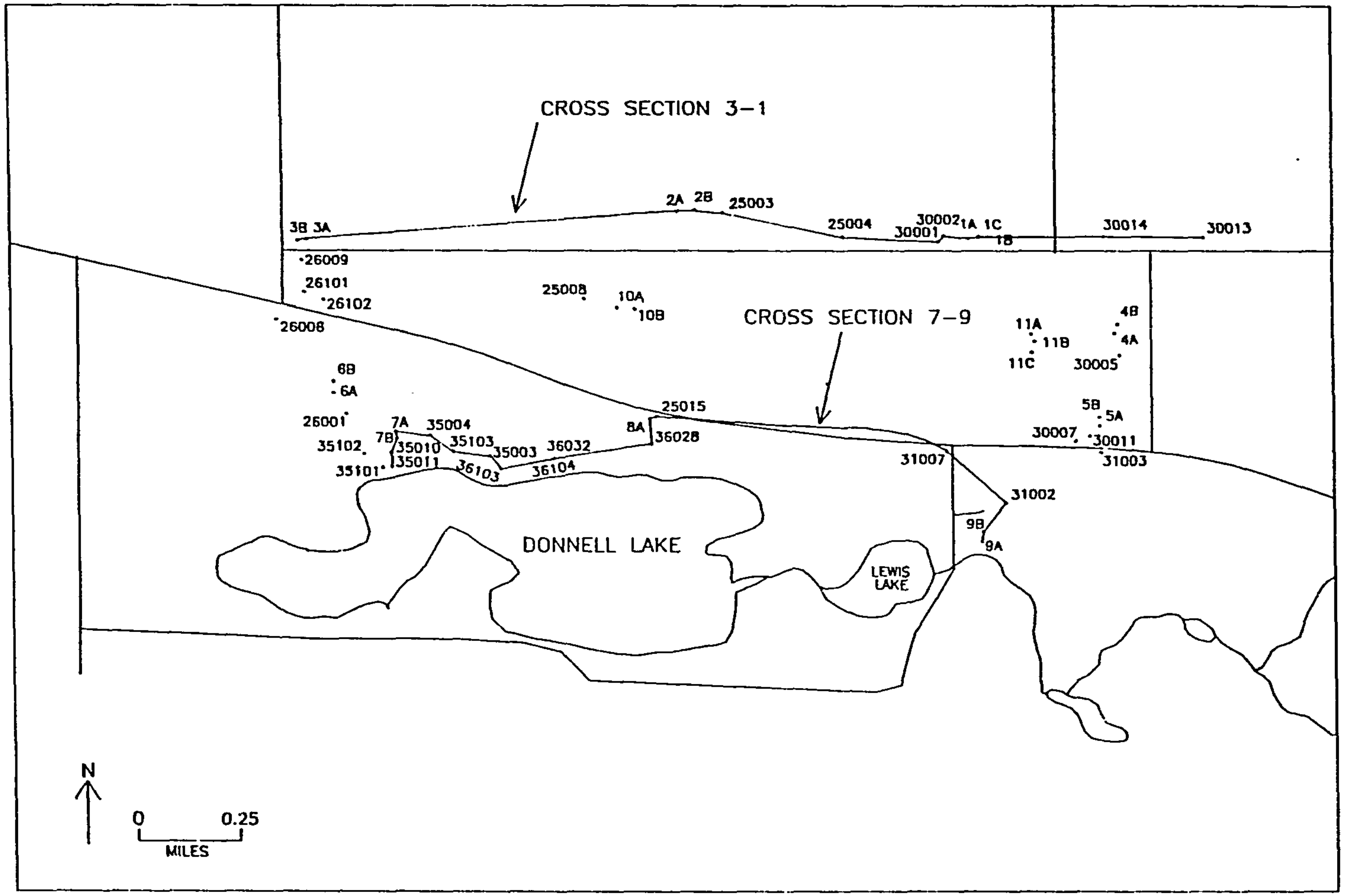


Figure 6. Location of East-West Cross Sections.

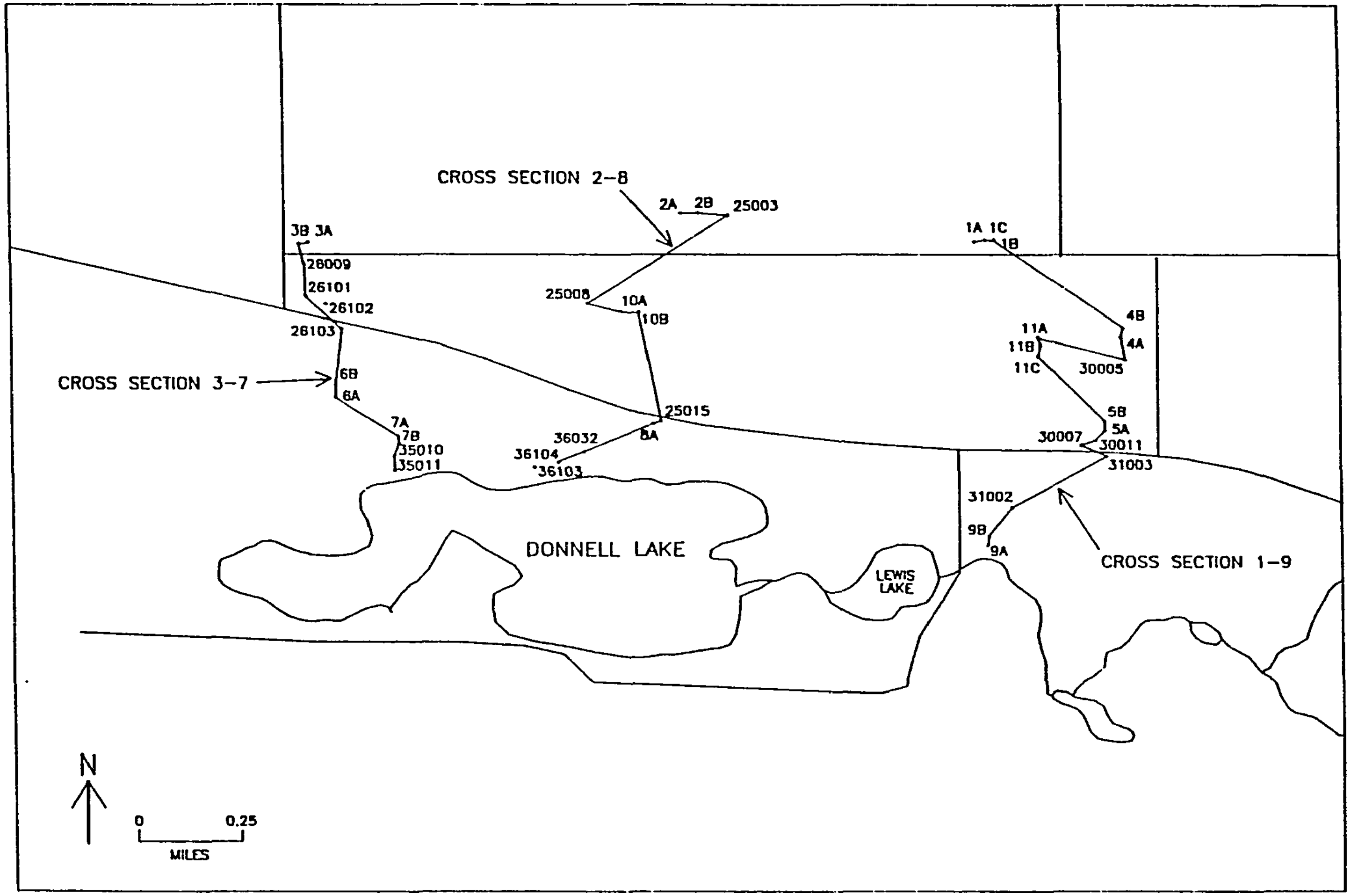


Figure 7. Location of North-South Cross Sections.

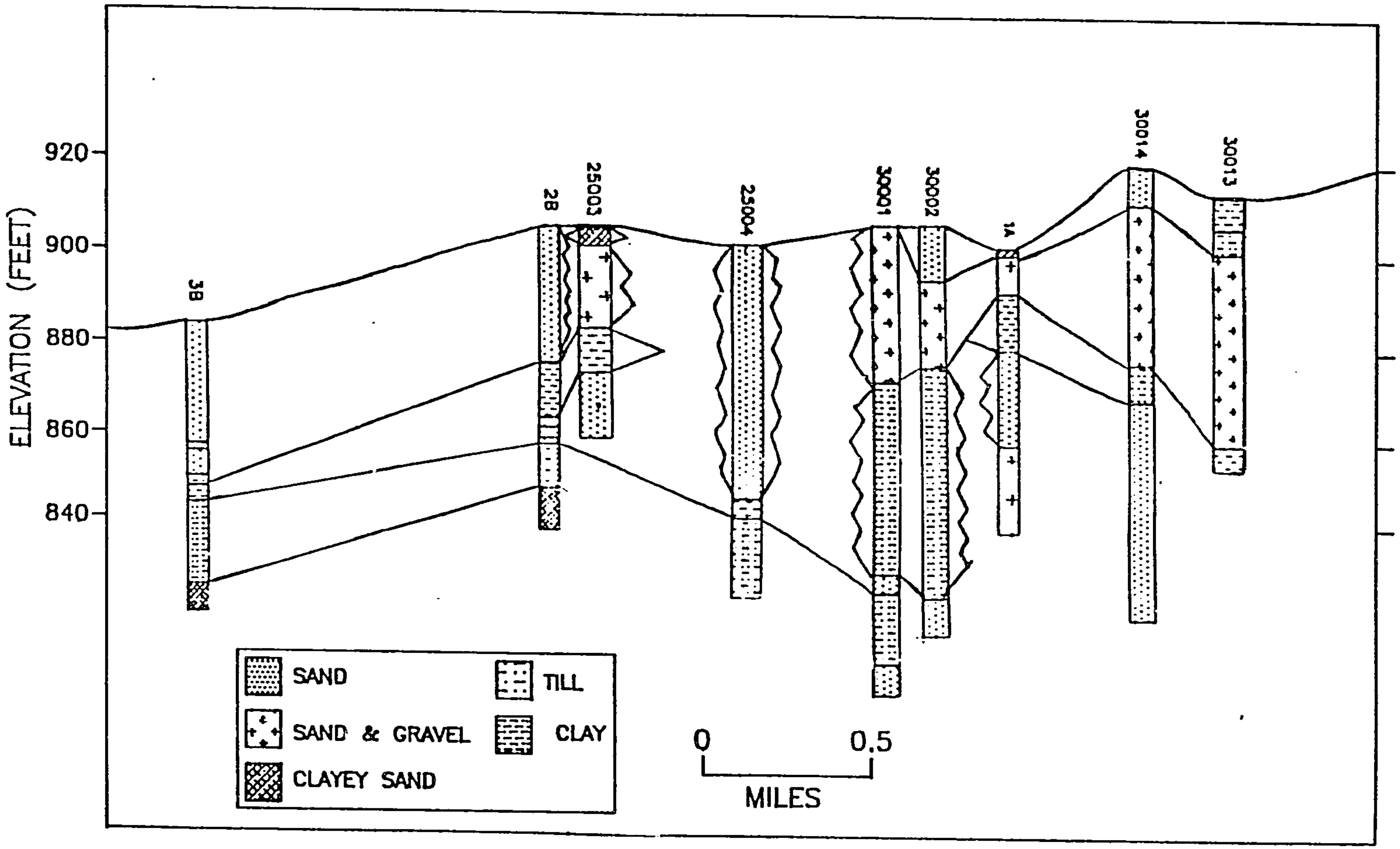


Figure 8. Geologic Cross Section 3-1.

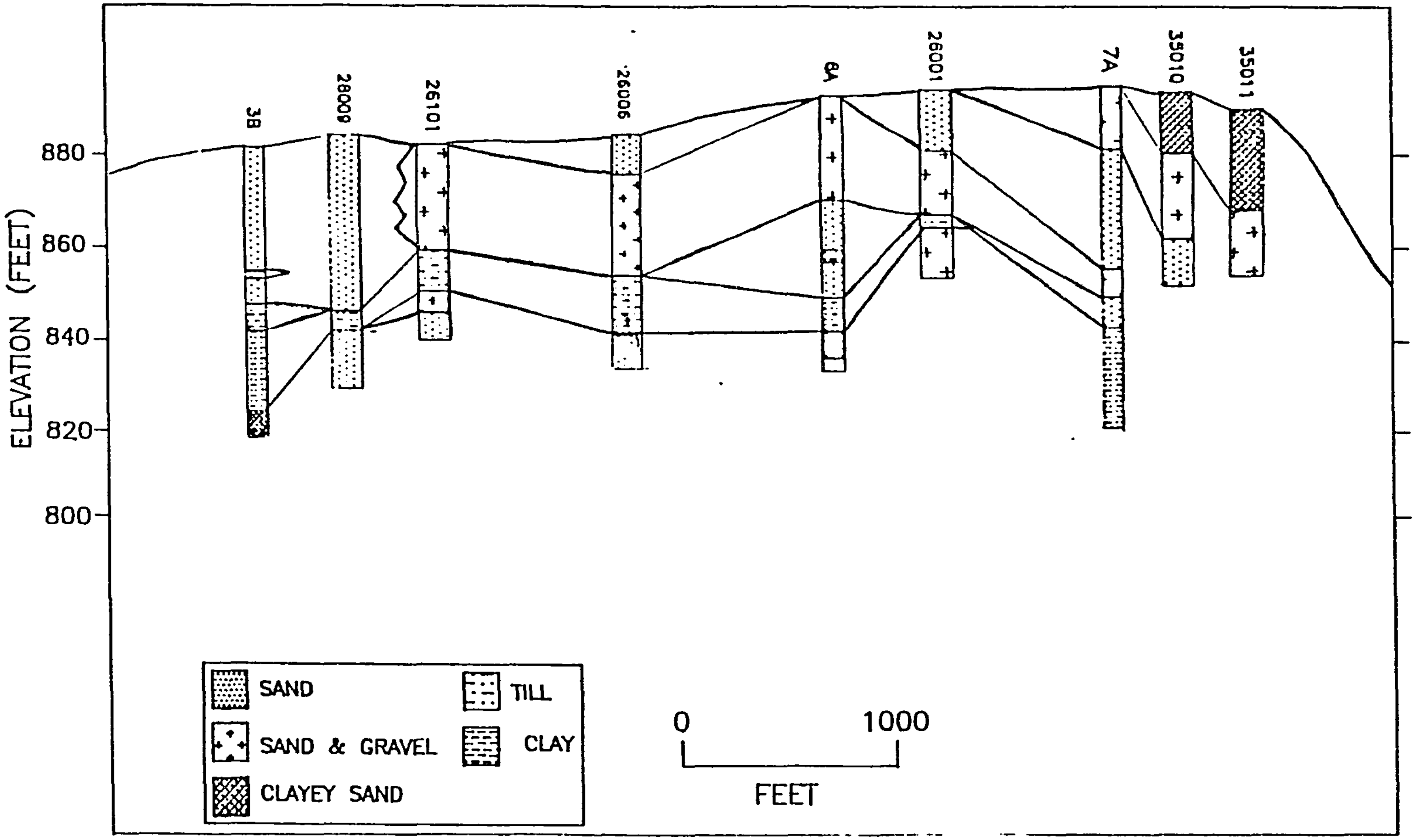


Figure 9. Geologic Cross Section 3-7.

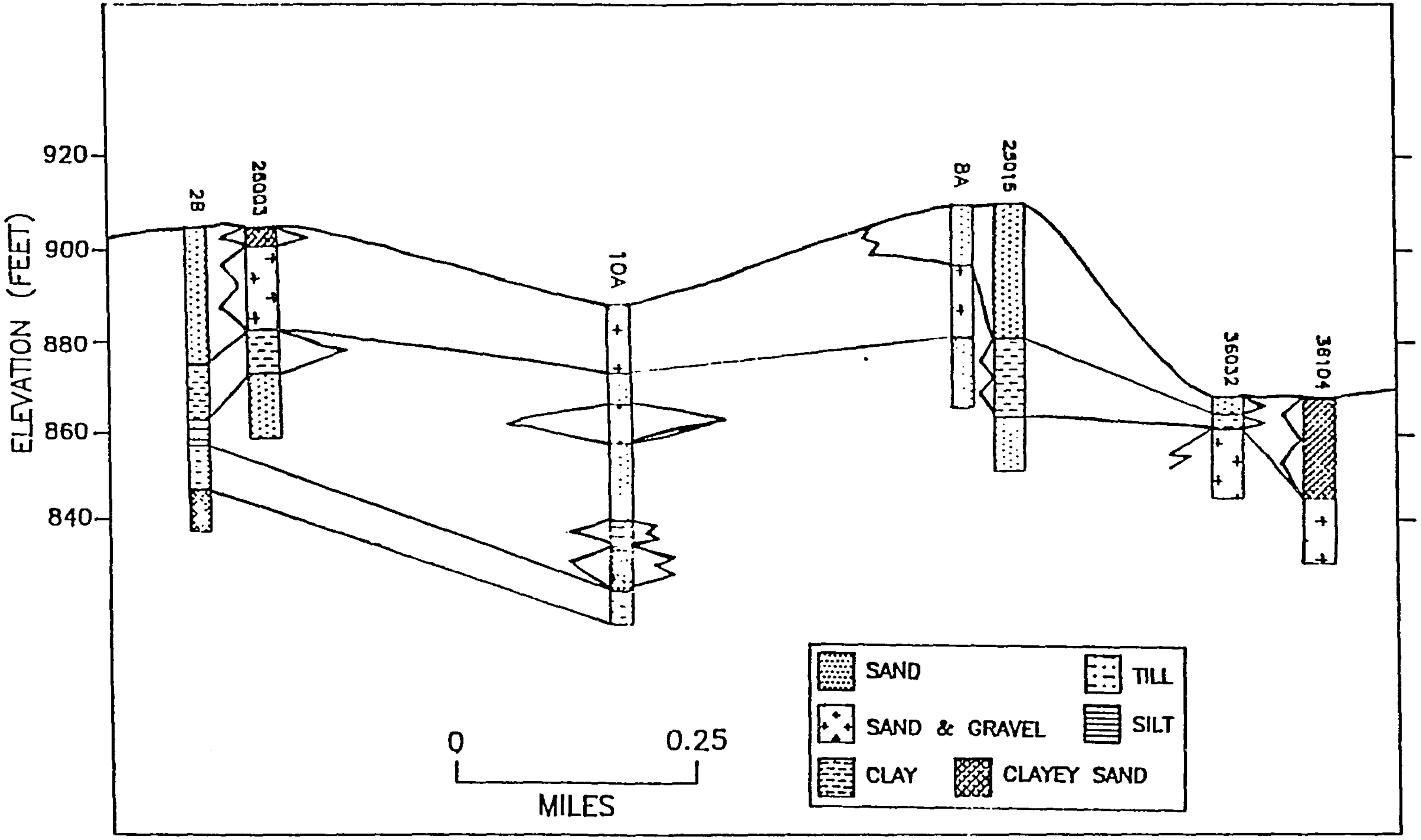


Figure 10. Geologic Cross Section 2-8.

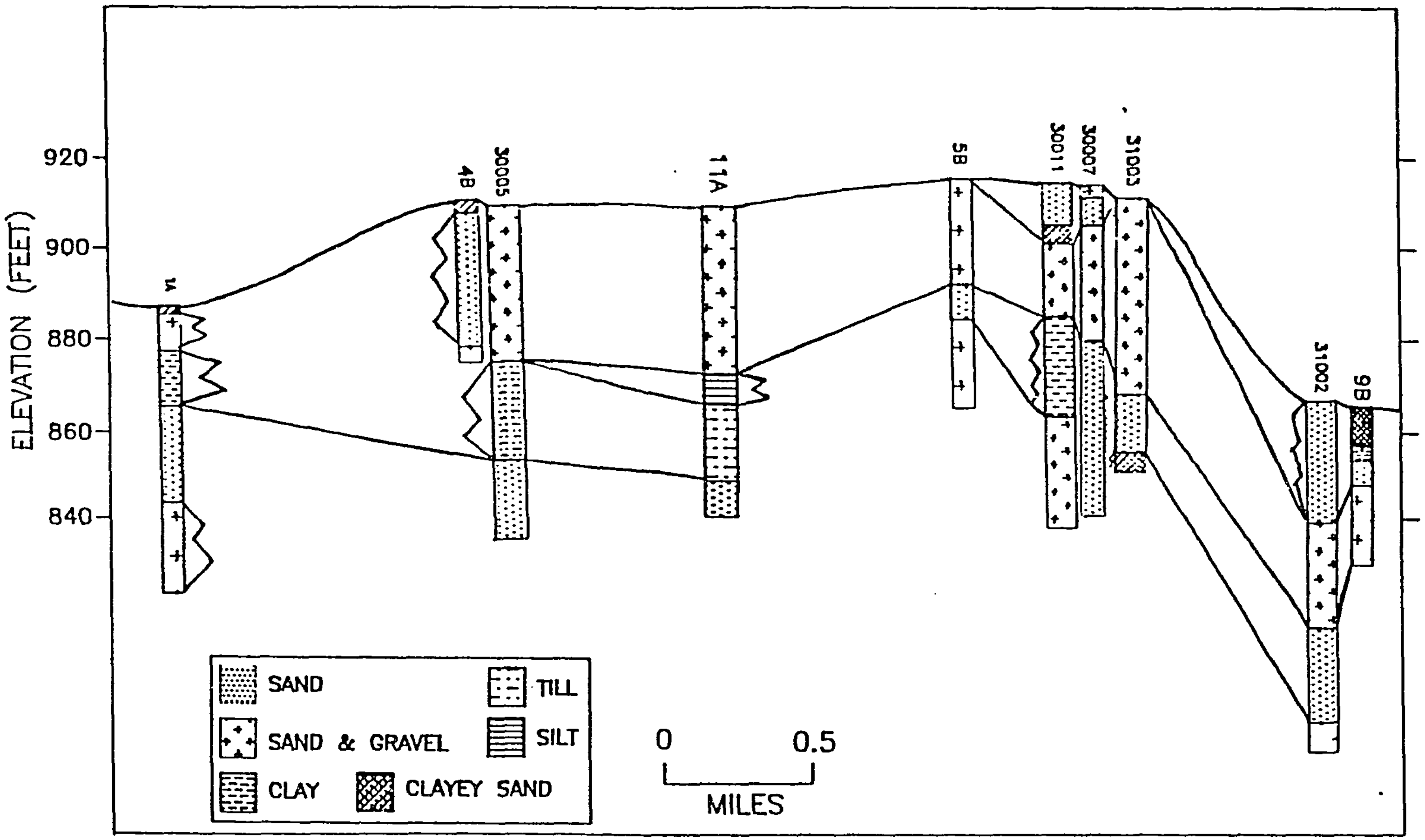


Figure 11. Geologic Cross Section 1-9.

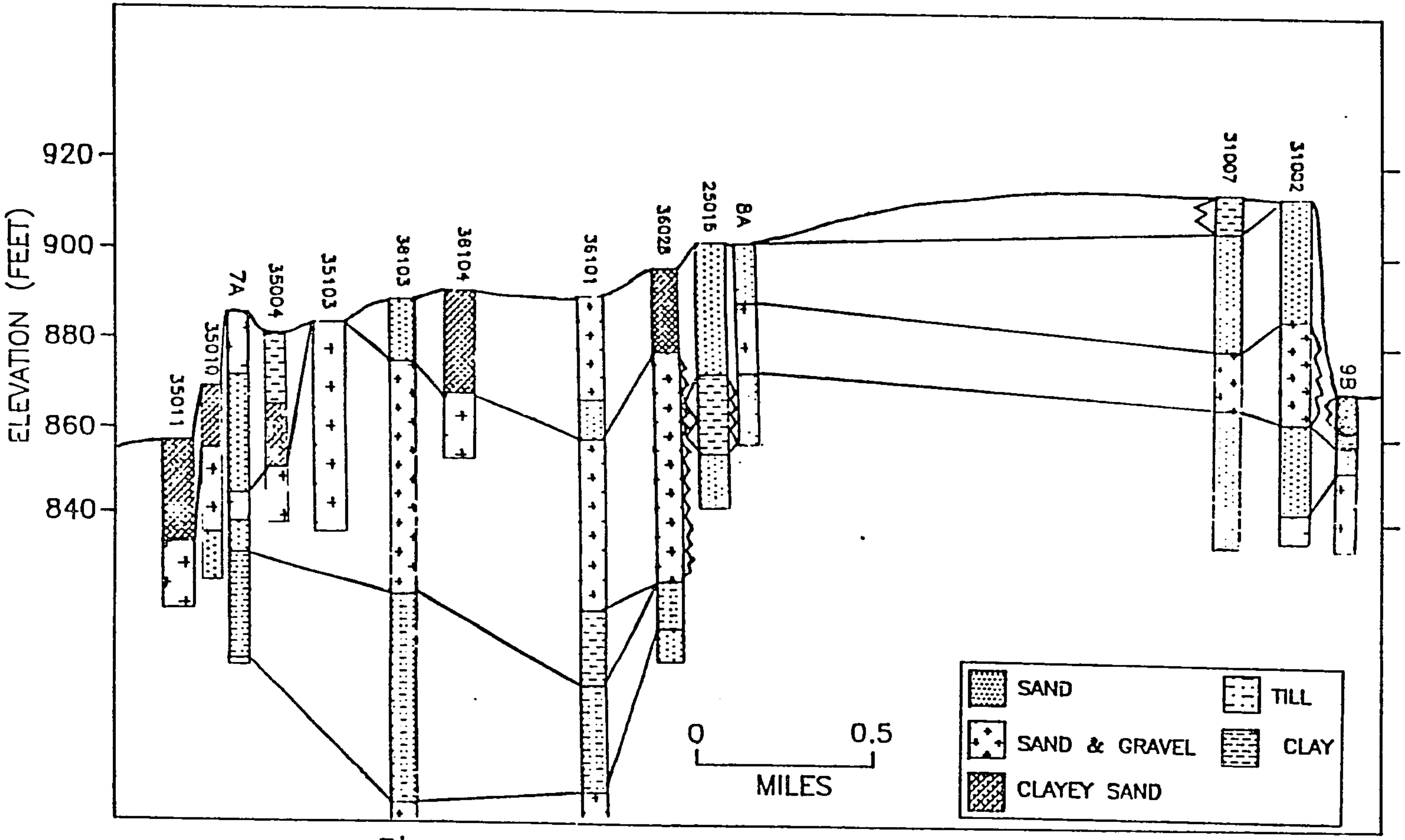


Figure 12. Geologic Cross Section 7-9.

along with residential well logs. Gamma ray logs and stratigraphic cross sections of WMU monitoring wells are located in Appendix A. The cross sections show vertical and lateral changes in stratigraphy throughout the study site.

Cross section 3-1 (Fig.8) shows an upper clay layer discontinuous east of well 25003. A lower till layer exists from 3A to 30001 and likely continues to the east and south in correlation with drilling logs. A thick till layer is recorded for wells 30001 and 30002 and, because it is not observed to the east, west, or south, may be due to incorrect sample interpretations. Alternating layers of sand and gravel compose the remainder of the stratigraphy.

Cross section 3-7 (Fig.9) shows the same lower till continuous from 3B to 7A and likely extending to the south beneath Donnell Lake. The upper clay layer encountered in cross section 3-1 appears to pinch out towards the south of well 3B. Sand and gravel comprise the remainder of the stratigraphy.

As in cross section 3-7, cross section 2-8 (Fig.10) shows the upper clay layer pinching out towards the east as well as the lower till layer gradually sloping towards the south. Sand and gravel compose the remainder of the cross section.

In cross section 1-9 (Fig. 11), the upper clay layer is present in well 1A; however, the lower till is not present and most likely lies below the 1A bore hole as indicated by drilling records to the east of 1A. The till layer is observed in 30005 and 11A and most likely dips below the remainder of the cross section wells consistent with the slopes of the till layer seen in cross sections 2-8 and 3-7. Sand and gravel comprise the remainder of the cross section.

Cross section 7-9 (Fig. 12) ties together the area geology and shows the lower till layer continuous from 7A to 36028 and likely continuing below the wells to the east of 36028. Sands and gravel compose the remainder of the stratigraphy.

The lower till layer can be correlated from all the cross sections and is shown as an areally continuous layer (Fig. 13). Elevation of the till layer varies from 860 feet in the northern part of the area to 800 feet near the north edge of Donnell Lake with thickness ranging from 3 to 26 feet. The till layer has a definite effect upon the water chemistry of the shallow aquifer.

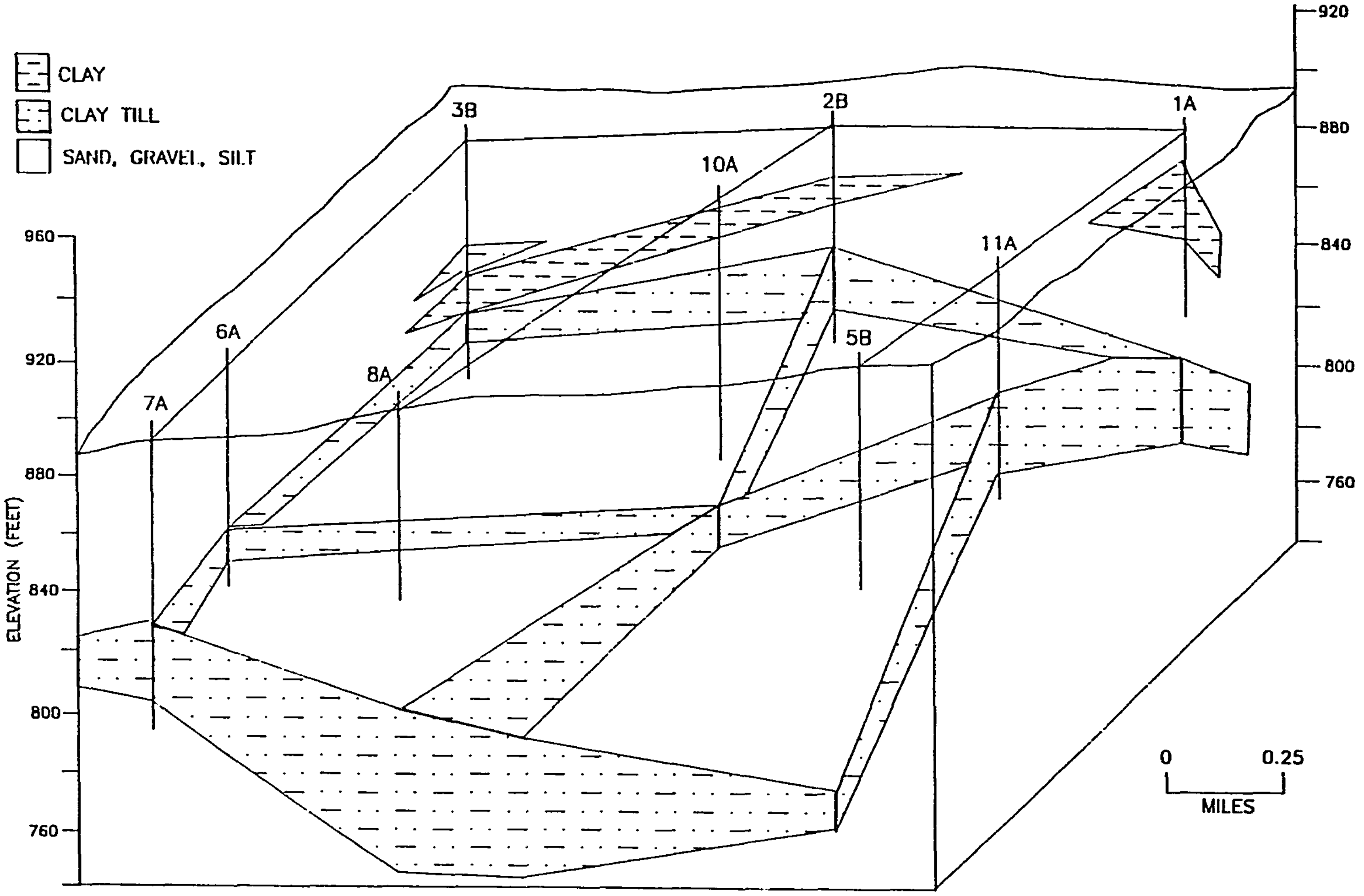


Figure 13. Fence Diagram of Till and Clay Layers.

HYDROLOGY

The surface water hydrology in the Donnell Lake area is characterized by east to west flow through a series of kettle lakes within the watershed boundary (Fig. 14). Flow from the east continues through Lewis Lake and Donnell Lake. Surface flow drains from the watershed through the southwest end of Donnell Lake into Paradise Lake and then continues into the Christiana Creek network. Christiana Creek joins the St. Joseph River and drains into Lake Michigan.

Local shallow ground-water flow is consistent with the watershed topography. The direction of flow is from the topographic highs continuing downgradient. Shallow flow discharges to the surface water bodies and continues towards the watershed drainage boundary near the southwest end of Donnell Lake. Local flow gradients vary around Donnell Lake with highest gradients found within areas of high topographic relief. Static water levels from monitoring wells were supplemented with domestic wells to construct a potentiometric surface (Fig. 14). The potentiometric surface was mapped using head values from shallow wells screened above till or clay layers to give accurate water table values. Ground-water flow regime zones were mapped using head values from every well in each well nest

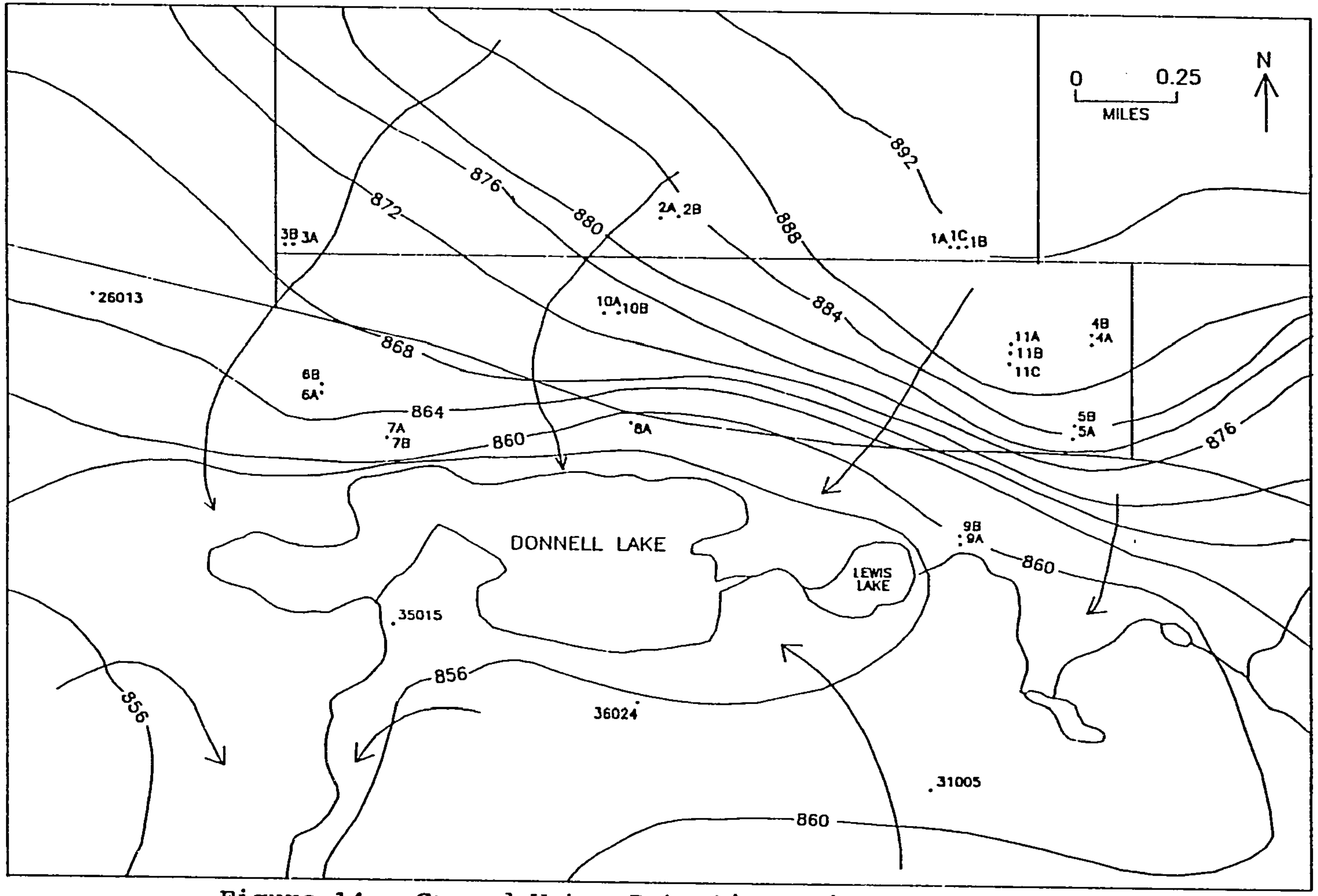


Figure 14. Ground-Water Potentiometric Surface Map.

(Fig. 15). As expected, the flow characteristics change from recharge in the higher surrounding areas to discharge near Donnell Lake.

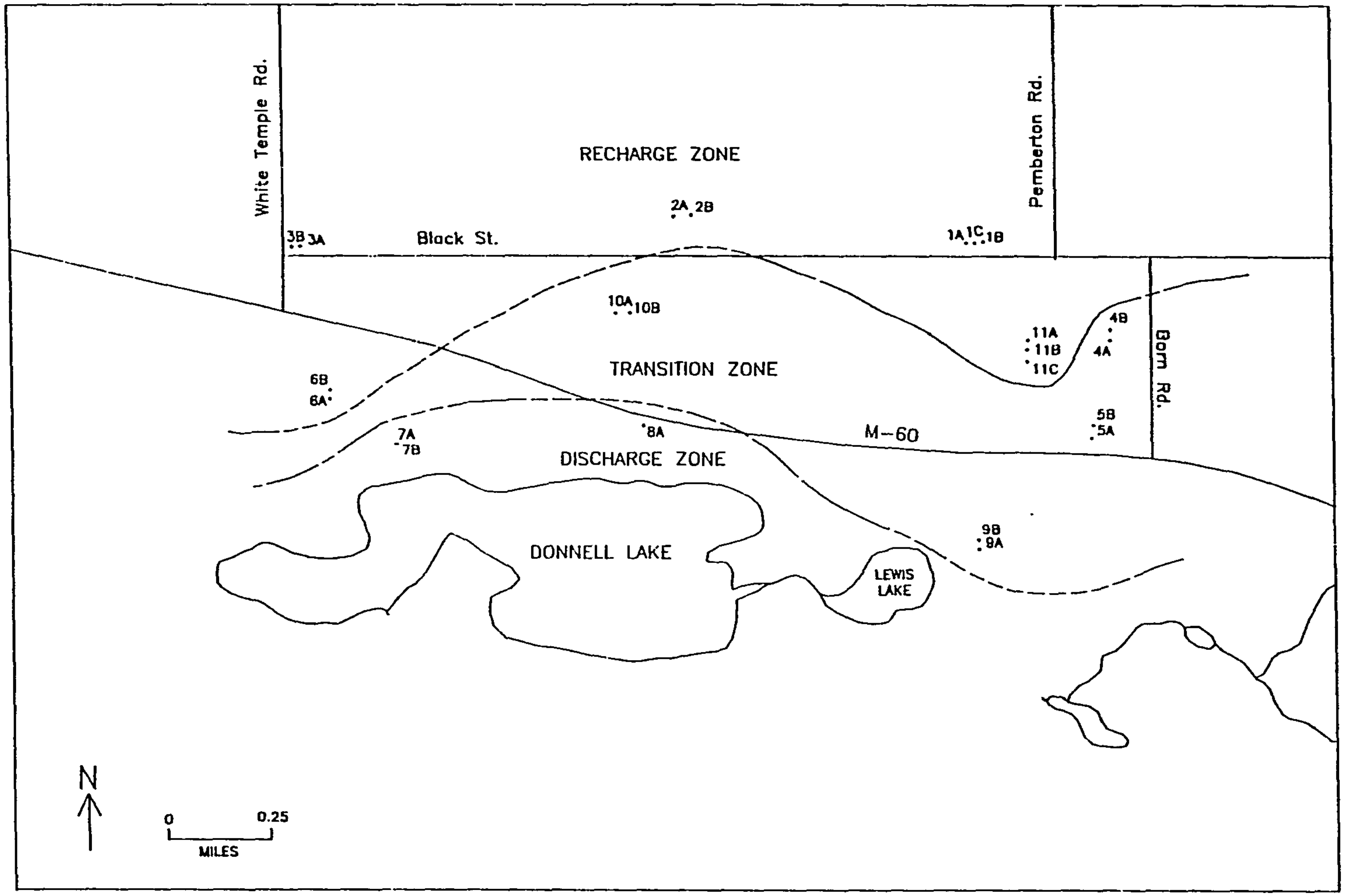


Figure 15. Ground-Water Flow Pattern.

NITROGEN

Occurrence

Nitrogen is one of the most abundant elements within the earth's biosphere. The availability of nitrogen and its compounds is essential for biologic productivity, and addition of natural or artificial nitrogen fertilizers in agricultural practices can produce greater crop yields. However, studies show a rise of nitrogen pollution in the last few decades affecting much of our surface and groundwater supplies. The nitrogen compounds (primarily nitrate (NO_3^-)) in soil and water come from various sources such as fertilizers, legume fixation, septic systems, storm runoff, and livestock manures.

In surface water increased nitrogen input could lead to eutrophication which alters the chemical and physical characteristics of the water body. Influx of nitrogen and other nutrients causes an increase in algae and bacteria production which in turn causes a large decrease in dissolved oxygen. Low oxygen makes the water body unfit for most fish and other organisms. Eutrophication is not easily reversed and is a threat to surface water quality in areas of high nutrient runoff.

Nitrogen compounds can also leach into ground water and lower water quality. The contamination of surface and ground water by nitrate threatens a small, yet important portion of our municipal, industrial, and residential water supply. The problem is of greater concern for the roughly 40 million people using water from private wells, many of whom are in rural, agriculturally dominated areas where nitrate contamination is likely to occur. Furthermore, regulated testing of private well water quality is not required as is with public water supply facilities.

A study in 1990 by the Monsanto Agricultural Products Company was done to investigate nitrate contamination in both private and public sources within agriculturally dominated areas in 26 states. Results showed that nitrate concentrations exceeded the maximum contaminant level (MCL) of 10 mg/L NO_3-N in 5% of the wells tested. Of the wells tested, 19% contained between 3 and 10 mg/L NO_3-N (USDA, 1991). A study done by the USEPA from 1988-1990 of 94,600 public wells and 10.5 million private wells showed that 1.2% of the public and 2.4% of the private wells contained nitrate above the MCL (USDA, 1991). The difference in the two studies is a result of the preferential sampling locations in the Monsanto study.

The occurrence of high nitrate levels in public drinking water supplies was also studied by Wade Miller Associates, Inc. A 1990 report concludes that, of 219 million people using public drinking water supplies, 1.7

million are exposed to nitrate levels above the MCL (U.S. Congress). This percentage (0.8%) is slightly less than the EPA study but still includes a considerable part of the population using water typically thought to be safe. In a June, 1990 report the General Accounting Office stated: "some drinking water violations are probably going undetected and unreported, and enforcement actions by the states are often inadequate" (Parry, 1990).

Health Hazards From Nitrate Exposure

The results of exposure to nitrates are still not well known. Physiological studies have been done to determine the effects of nitrates, which are not only found in water supplies, but are also used as preservatives in food. A well known illness caused by high nitrate exposure is methemoglobinemia, or "blue-baby syndrome". Methemoglobinemia is usually limited to infants under 6 months of age. In the first few months, the relatively low acidity of a baby's stomach is unable to inhibit bacterial conversion of nitrate to toxic nitrite. Nitrite couples with hemoglobin and reduces the oxygen-carrying capacity of the blood. The resulting asphyxiation causes a skin color change which gives the disease its nickname. Fortunately, methemoglobinemia is rarely fatal and can be easily treated (National Research Council, 1978).

Even in adults, nitrate can be internally converted to nitrite. Coupling of nitrite with secondary and tertiary amines produces nitrosamines which are known carcinogens capable of causing tumors in nearly all organs in animal tests at high doses. Tumors in humans have not been proven to be a result of nitrosamines and epidemiological studies do not give an accurate measure of exposures required to produce tumors. However, Bouwer (1990) reports a strong geographical correlation between nitrate intake and gastric cancer. Japan has the highest nitrate intake and also the highest incidence of gastric cancer while the United States has the lowest in both categories.

Nitrate Loading to Ground Water

The ability for nitrate or other forms of nitrogen to enter the ground-water system is dependent on surface and vadose zone conditions. The nitrogen cycle depicts mass balance partitioning of nitrogen compounds between atmospheric, terrestrial, and aquatic systems (Fig. 16).

Atmospheric nitrogen (N_2, N_2O, NH_3) can be incorporated (or fixed) into the soil. Depending on soil conditions, nitrogen can be assimilated into plant tissue, sorbed onto the soil mass, or oxidized into a mobile anionic form easily leached into the vadose zone. These processes can also be reversed maintaining mass balance. Nitrification is the primary process for transformation of nitrogen compounds into nitrate. Nitrification converts ammonia, which is volatile but also very sorptive, and organic nitrogen compounds into nitrate. This process occurs almost solely by bacterial mediation within the soil zone. Nitrite is produced in an intermediate step in nitrification but is rapidly consumed as bacteria obtain most of their energy from oxidation of nitrite to nitrate. This is one reason nitrite is often at undetectable concentrations in ground water. These nitrifying organisms are found throughout soil and aquatic systems and, although mesophilic in nature (optimum temp.= 30 deg. celsius, optimum pH = 8.0), have been found in a wide range of conditions (National Research Council, 1978).

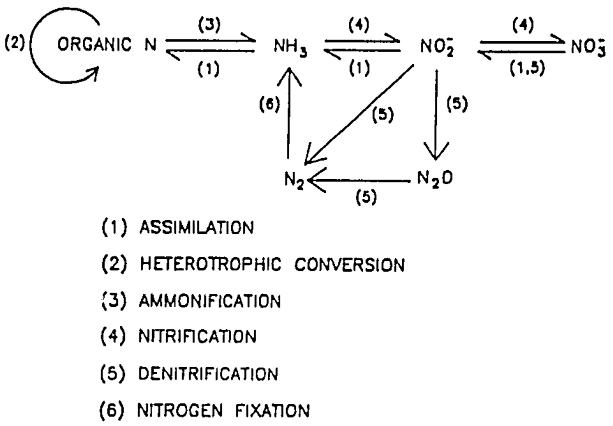


Figure 16. Biological Nitrogen Cycle.

Nitrate Loading From Agriculture

Loading of nitrate to water systems in agricultural settings is mainly a result of leaching of applied nitrogen fertilizers. High nitrogen fertilizers are usually applied as nitrate-ammonium, urea, manure, or anhydrous ammonia. Nitrogen fertilizers readily dissociate and ideally the nitrogen compounds, nitrate and ammonium, are assimilated into plant tissue. Some studies have shown large losses of ammonium to volatilization before nitrification can occur when soil pH is high enough to favor dissociation of ammonium into volatile ammonia (Staver and Brinsfield, 1990). This can cause considerable loss from one area and addition to an adjacent area. A study by the U.S. Geological Survey done in Kalamazoo County, Michigan estimated nearly 42% of nitrogen input to the soil zone is due to precipitation and dry fallout (Rheaume, 1990).

Once fertilizer is applied, several factors influence the process of crop uptake. The ability of the soil to receive, store, and transmit water and the extent of irrigation and precipitation will determine the amount of nitrogen assimilated by the crops and the amount leached through the soil zone. Often, excess fertilizer applications along with over-irrigation to produce optimum yields enhance leaching. Use of nitrogen fertilizers increased from 2.8 to 11.9 million tons a year from the years 1960 to

1981 mainly due to increased application rates per acre (USDA, 1991). Some studies have shown up to 50% of applied fertilizer is leached from the soil zone into ground water due to excess fertilization and over-irrigation (Exner and Spalding, 1979). Denitrification in the vadose zone is rare, and, in particularly sandy soils such as the soils in the Donnell lake area, denitrification is virtually nonexistent (Saffigna and Keeney, 1977). Transport time through the vadose zone to the saturated zone (lag time) will determine seasonal appearance of nitrate in the ground water. Nitrate levels in the soil are typically highest in late summer resulting from fertilization and microbial release of nitrogen compounds (Staver and Brinsfield, 1990). Lag time depends on the substance being leached, vadose zone material, and vadose zone thickness and may vary from hours to years (Hubbard, Asmussen, and Allison, 1984).

Nitrate Loading From Livestock Practices

Nitrate loading from livestock facilities results from infiltration of breakdown products from animal waste. Waste products also contain large amounts of bacteria, but, with a short life-span outside the host, migration of bacteria to the saturated zone is unlikely. The high level of nitrogen compounds in livestock waste is a result of inefficient conversion of feed protein. The results of one year-long study showed 24.6 megatons of grain and vegetable protein produced in the United States (91% of total production) is used as feed to produce 5.3 megatons of animal protein (National Research Council, 1978). The remainder of the protein is excreted as waste. Nitrogen in the waste is partitioned between feces and urine. For swine, 72% of the nitrogen is excreted as urine. With 70-75% of the nitrogen in feeds appearing in waste products, the annual waste nitrogen production of one pig is estimated at 6.5 to 7.5 kg (National Research Council, 1978). This can add considerable amounts of nitrogen to the surface in places of high hog density such as Cass, Ottawa, and Allegan Counties in southwestern Michigan where a majority of the 1.3 million hogs in Michigan are located (Shaffer and VanderMeulen, 1987).

The amount of leaching from feedlots depends on animal density, vegetation present, and the chemical and physical conditions within the soil zone.

Grazing animals typically devour any plant matter available, and therefore nitrogen uptake by vegetation is slight. One study showed leaching increased 5.6 times on land grazed by cattle compared to land cut but ungrazed (Hubbard and Sheridan, 1989). Soil conditions in feedlots determine the fate of waste nitrogen. Under warm, wet conditions, urea hydrolyzes to NH_3 and CO_2, with the NH_3 readily volatilizing. Studies show losses of total nitrogen from urine volatilization are from 25% to 90% (National Research Council, 1978). As with volatilization losses from fertilizer, uptake of ammonia from waste products by wind currents can cause loading to nearby areas including lakes. The high ammonia concentrations and high pH in feedlot soil initially delay nitrification by slowing bacterial activity. When a feedlot is taken out of use, chemical and physical characteristics of the soil change, and nitrification and subsequent leaching is rapid.

Confinement and semi-confinement facilities can reduce the amount of waste runoff and percolation through the soil zone. Waste is collected and used as manure fertilizer on crop fields. Although collection of animal waste reduces nitrate leaching in the livestock area, ammonia volatilization occurs readily during storage, handling, and spreading of the manure. Studies show up to 50% of the total nitrogen in collected manure is lost as ammonia (National Research Council, 1978). Much of the loss is due to time of fertilizer application. Manure is often applied in the early spring before planting resulting in increased volatilization as well as high runoff rates (Bouwer, 1990).

GROUND-WATER CHEMISTRY

General Chemistry

The major ion chemistry of the ground water in the Donnell Lake area is dominated by bicarbonate, calcium, magnesium, and sulfate. This association is typical of sand and gravel aquifers (Cummings, 1980). Water chemistry analysis results are shown in Table 2. Total dissolved solids (TDS) concentration lowered with increasing depth in nearly all of the well nests tested (Fig. 17). Well nests 3 and 11 show a slight increase in TDS with depth.

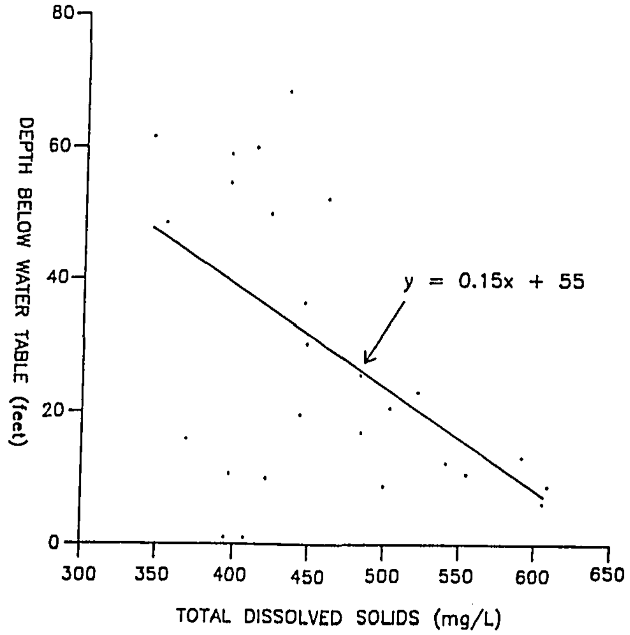


Figure 17. Total Dissolved Solids (mg/L) vs. Depth Below Water Table.

Table 2

Ground-Water Chemistry Analysis Results

Well	Depth (feet)*	pH	Temp. (Cel.)	Cond. (micromhos/cm)	Dissolved Oxygen (ppm)
1A	62	7.62	11.2	476	0.13
1B	30	7.47	10.8	682	5.1
1C	9	7.19	7.0	1064	5.7
25003	20	7.52	8.2	582	NA
2A	10	7.45	8.6	586	8.7
2B	59	7.49	9.2	509	0.12
26009	53	7.23	16.4	578	NA
3A	16	7.28	15.6	490	0.25
3B	60	7.48	16.3	513	0.12
30005	55	7.32	11.0	539	NA
4A	13	7.12	11.1	1090	6.45
4B	23	7.01	11.4	1013	7.3
5A	6	7.05	15.9	947	8.2
5B	26	7.29	16.0	714	4.8
26001	17	7.21	16.5	604	NA
6A	49	7.72	15.5	441	0.3
6B	11	7.54	15.8	513	7.1
35010	37	7.37	17.6	635	NA
7A	69	7.68	16.1	513	0.25
7B	12	7.27	16.6	656	6.9
25015	25	7.47	11.6	742	NA
8A	8	7.14	11.4	824	7.3
31002	30	7.62	12.4	495	NA
9A	14	7.41	14.6	537	4.3
9B	37	7.50	16.0	507	0.14
10A	64	7.41	11.8	540	0.2
10B	11	7.21	11.0	920	7.8
25008	18	7.41	14.4	602	NA
11A	50	7.59	11.1	514	0.15
11B	1	7.27	11.0	450	0.2
11C	21	7.12	11.2	630	0.18

NA = no data available
* Depth is feet below water table.

Table 2--continued

Well	Alkalinity (ppm $CaCO_3$)	Cl (mg/L)	SiO_2 (mg/L)	SO_4 (mg/L)	NH_3 (mg/L)	Fe (mg/L)	Mn (mg/L)
1A	170	<2.0	12.2	33.0	0.05	0.01	0.0
1B	230	7.5	16.0	26.1	0.016	0.0	0.0
1C	300	9.5	12.3	40.3	0.029	0.55	0.0
25003	220	3.5	12.7	47.7	0.011	0.05	0.0
2A	230	2.8	13.8	19.3	0.029	0.0	0.0
2B	200	2.4	16.6	47.2	0.072	0.33	0.0
26009	210	6.5	9.8	73.3	0.053	0.23	0.03
3A	170	9.5	9.4	48.9	0.265	1.02	0.14
3B	220	3.1	17.2	32.4	0.15	0.69	0.02
30005	181	3.8	11.1	51.6	0.032	0.81	0.0
4A	325	14.0	15.2	34.1	0.0	0.0	0.0
4B	230	14.0	15.3	31.8	0.023	0.3	0.0
5A	300	20.0	14.4	29.0	0.011	0.0	0.0
5B	250	10.4	13.7	26.1	0.037	0.0	0.0
26001	250	15.0	10.7	31.6	0.017	0.0	0.0
6A	190	2.7	14.6	20.0	0.108	0.0	0.01
6B	200	8.8	11.5	35.3	0.011	0.0	0.0
35010	260	11.0	13.8	34.2	0.0	0.0	0.0
7A	260	3.6	16.4	5.0	0.329	0.09	0.0
7B	290	18.0	14.4	20.2	0.0	0.0	0.0
25015	250	10.5	13.2	39.5	0.02	0.13	0.0
8A	235	15.0	12.8	41.6	0.0	0.0	0.0
31002	260	<2.0	15.4	4.4	0.102	0.0	0.0
9A	270	7.8	12.6	13.4	0.0	0.0	0.0
9B	270	5.5	15.0	0.1	0.299	1.55	0.0
10A	275	<2.0	16.2	12.4	0.193	0.0	0.0
10B	280	20.0	11.7	26.8	0.0	0.0	0.0
25008	240	4.4	13.7	27.6	0.032	0.21	0.0
11A	205	6.3	15.3	56.3	0.075	0.002	0.0
11B	250	4.5	10.9	0.0	1.3	6.29	0.2
11C	295	4.0	13.7	4.9	1.04	2.46	0.2

Table 2--continued

Well	NO_3-N (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)
1A	0.0	70.8	25.0	2.84	1.61
1B	11.5	91.6	36.2	3.14	1.83
1C	29.2	136.9	31.6	13.16	20.89
25003	4.0	87.0	30.8	3.21	1.54
2A	18.1	86.9	28.1	2.96	5.99
2B	0.0	73.0	26.9	3.25	1.70
26009	0.0	85.5	30.5	3.31	1.73
3A	0.5	74.5	23.3	2.13	1.72
3B	0.0	76.8	28.0	4.07	1.48
30005	0.0	79.7	27.4	4.04	1.45
4A	25.7	87.0	44.9	2.4	0.77
4B	26.5	138.6	36.4	13.29	9.40
5A	17.0	124.9	23.3	25.61	12.46
5B	11.9	98.0	32.5	7.77	2.62
26001	0.9	86.1	26.8	10.82	1.94
6A	0.4	68.1	24.6	6.58	2.28
6B	1.2	73.9	25.5	5.95	1.66
35010	1.8	0.3	0.0	151.10	0.44
7A	0.1	72.1	27.6	6.54	1.79
7B	1.2	91.7	26.9	16.08	2.19
25015	11.0	0.6	0.0	181.50	0.63
8A	17.8	103.1	38.8	10.76	3.23
31002	0.0	0.4	0.0	135.50	0.75
9A	0.5	84.2	28.9	4.47	1.78
9B	0.0	79.1	27.3	5.09	1.61
10A	0.0	79.7	34.7	5.22	1.83
10B	20.4	119.8	31.9	10.64	8.53
25008	6.7	91.8	33.3	4.01	1.79
11A	0.0	79.1	28.0	5.03	1.78
11B	1.1	73.6	19.6	2.45	1.87
11C	0.0	96.9	31.2	5.48	2.41

Mass balance errors show change with depth throughout the Donnell Lake area (Table 3). A definite trend of increasing mass balance error (difference in anion and cation totals for an individual sample) with decreasing TDS (or increasing depth) is shown in well nests 1, 4, 5, 6, 7, and 8. Well nests 2, 3, 4, 10, and 11 show a mass balance error increase from the shallow to the deep well, however, the intermediate well does not follow the trend. Only nest 9 shows a net decrease in mass balance error with depth. Mass balance error averages for ground-water chemical analyses are 4.3%, 8.0%, and 10.6% for shallow, intermediate, and deep wells, respectively. A reason for consistently higher mass balance errors in deeper wells is not clear.

Well nests showing low or no contamination impact give similar patterns in mass balance error change with depth as did the nests with sharp vertical decreases in contamination. However, shallow wells with little or no contamination effects show higher mass balance errors than do shallow wells with large contamination effects.

Both total cations and total anions decrease with increasing depth. Distribution among individual cations remains fairly constant with only sodium showing a mass increase with depth relative to total cationic mass. Anionic distribution shows a definite change with depth. Nitrate and chloride both make up a considerable share of

Table 3

Mass Balance Calculations From Ground-Water Quality Results

Well ID	Depth (feet)	Anion Total (meq/l)	Cation Total (meq/l)	Mass Balance Error (%)
1A	62	4.256	5.766	15.1
1B	30	6.503	7.732	8.6
1C	9	10.263	10.557	1.4
25003	20	5.898	7.056	8.9
2A	10	5.879	6.930	8.2
2B	59	5.067	6.052	8.9
26009	53	6.008	6.972	7.4
3A	16	4.828	5.808	9.2
3B	60	5.159	6.376	10.5
30005	55	5.061	6.473	12.2
4A	13	8.478	8.159	-1.9
4B	23	9.965	10.740	3.7
5A	6	9.130	9.585	2.4
5B	26	6.995	7.969	6.5
26001	17	6.627	7.022	2.9
6A	49	4.273	5.767	14.9
6B	11	5.145	6.087	8.4
35010	37	6.405	6.597	1.5
7A	69	5.435	6.202	6.6
7B	12	7.326	7.544	1.5
25015	25	6.904	7.944	7.0
8A	8	8.065	8.887	4.9
31002	30	5.281	5.932	5.8
9A	14	5.951	6.819	6.8
9B	37	5.618	6.360	6.2
10A	64	5.805	6.964	9.1
10B	11	9.322	9.192	-0.7
25008	18	6.165	7.452	9.4
11A	50	5.526	6.376	7.1
11B	1	5.226	5.640	3.8
11C	21	6.189	7.657	10.6

* feet below static water table

total anions in shallow and intermediate wells decreasing slightly in total mass from shallow to intermediate depths. Both nitrate and chloride concentrations drop sharply from intermediate to deep well depths. This change in anion partitioning can be tied directly to surficial input. Nitrate and chloride are limited to the upper zone of the aquifer as a result of infiltration location, flow patterns, and aquifer stratigraphy. Along with obvious surficial source constituents such as nitrate, chloride, and potassium, the relatively high TDS at low and intermediate depths is a result of direct and indirect surface contamination. High TDS values are common within shallow regions of unconfined aquifers at sites of known contamination impact (Rheaume, 1990). As expected, conductivity also decreases with increasing depth being a direct function of TDS (Fig. 18).

Dissolved oxygen results show an exponential decrease with depth (Fig. 19). Included in the dissolved oxygen data was an air-water equilibrium endpoint using the average water temperature for shallow wells. This assumes water throughout the vadose zone is at equilibrium with atmospheric oxygen (White, Peterson, and Solbau, 1990). Well nests 11 and 9 were exceptions showing both low values in dissolved oxygen and TDS in the shallow and intermediate wells. The low values from 11B are a result of a highly eutrophic wetland area directly upgradient of well nest 11.

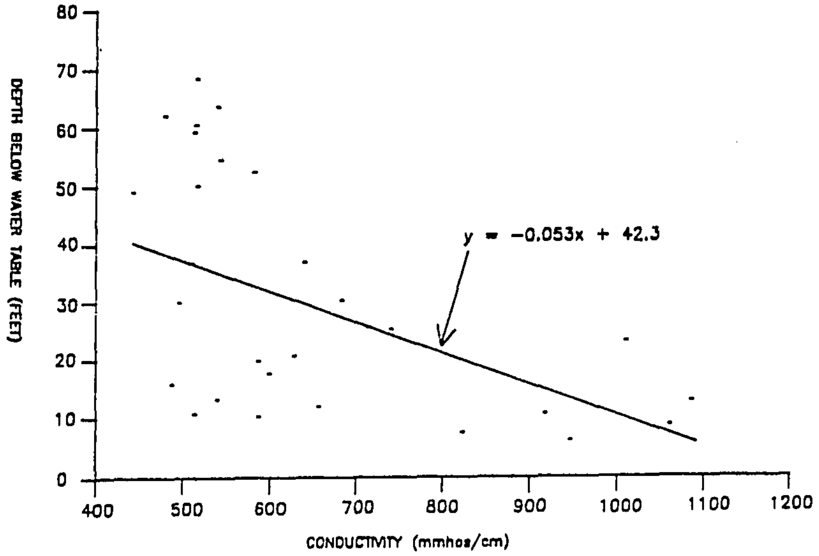


Figure 18. Conductivity vs. Depth Below Water Table.

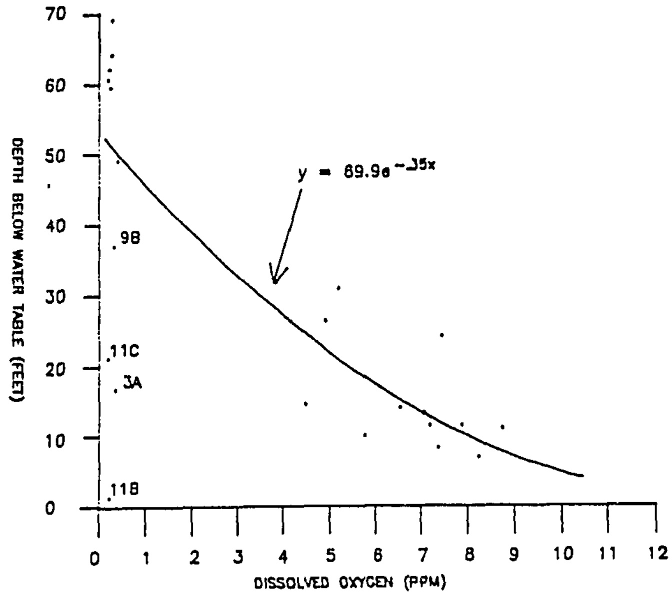


Figure 19. Dissolved Oxygen vs. Depth Below Water Table.

This wetland can be seen in the isoconcentration maps. The wetland receives direct runoff from livestock facilities and croplands. Highly reduced water from the wetland discharges to the south towards well nest 11 (Fig. 14). Relatively low values for nitrate, sulfate, and dissolved oxygen coupled with high ammonia and iron concentrations in well 11B and 11C (1 ft. and 21 ft. below water table, respectively) suggest infiltration of reduced surface water into shallow ground water to produce this localized effect. Well 9B (37 ft. below water table) shows the same increases in ammonia and iron along with near detection limit readings for nitrate, sulfate, and dissolved oxygen. However, these conditions are not present in 9A (14 ft. below water table). The chemical characteristics of well 9B may be caused by redox changes with path length as seen in well 7A and not infiltration of reducing water. Conditions often become more reducing with path length and the redox chemistry in the deep wells and most of the intermediate wells cannot be directly correlated to contamination input.

Some of the shallow and intermediate wells show relatively high values for chloride. Figure 20 shows chloride concentrations for shallow wells. Wells 1C, 4A, 4B, 5A, 26003, 7B, 8A, and 10B show anomalously high chloride concentrations. Most of these wells also contain relatively high values for sodium indicating runoff and

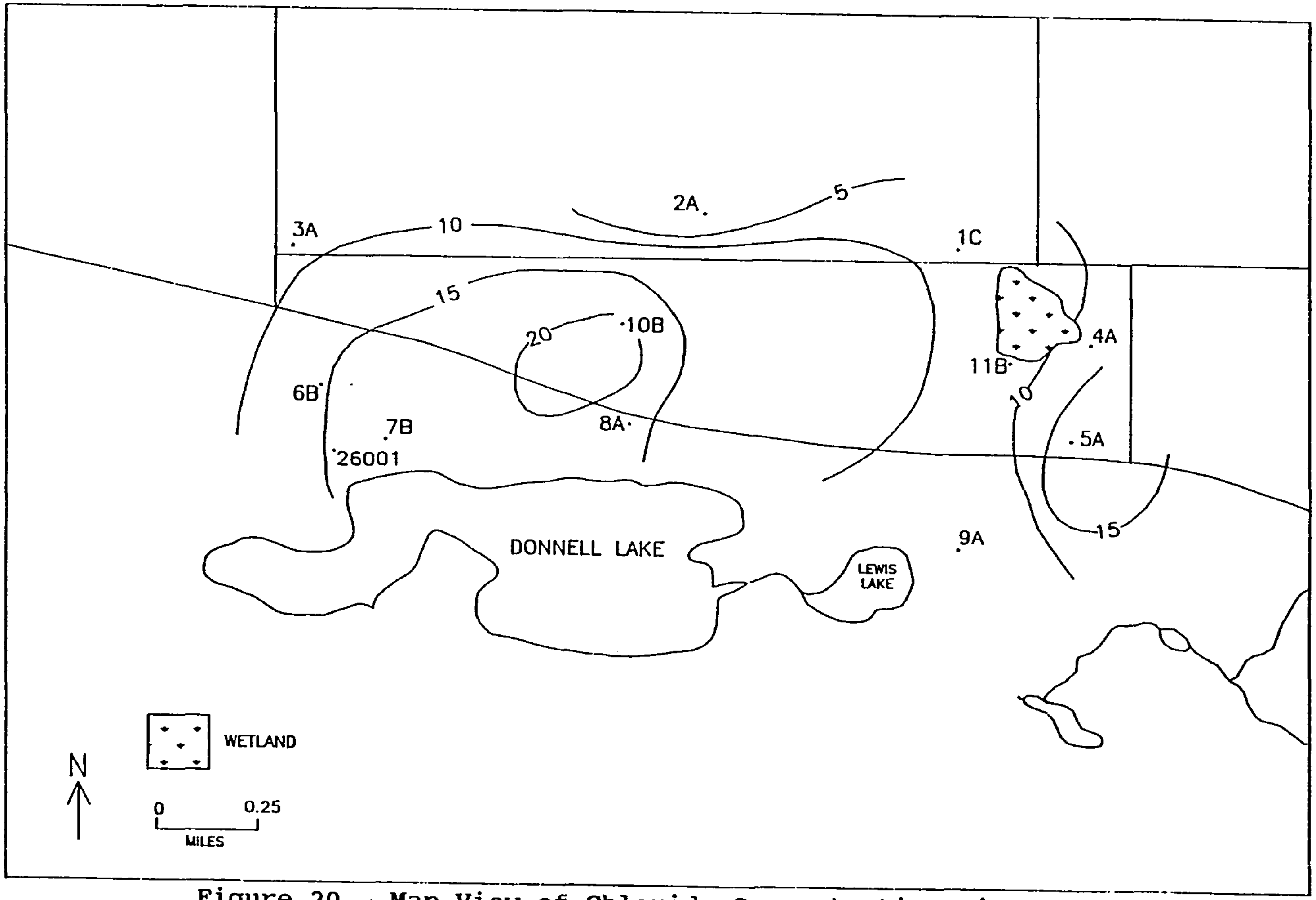


Figure 20. Map View of Chloride Concentrations in mg/L for Shallow Wells.

infiltration of road salt. All wells high in chloride except 10B are located near roads likely salted during the winter. Well 10B is located in a topographic low between M-60 and Black Street and may be receiving road salt runoff from either of these roads.

Wells 35010, 25015, and 31002 show very high values for sodium along with low magnesium and calcium concentrations indicating treatment with a water softener. These wells are deep enough that road salt contamination is unlikely. Contamination from road salt depends on distance from roadways and location with respect to the ground-water gradient. Wells 1C and 3A are located upgradient but are close enough in proximity to Black Street to receive salt runoff.

Nitrate concentrations were highest within the flow path extending from crop fields and swine holdings decreasing with depth and flow path length (Fig. 21).

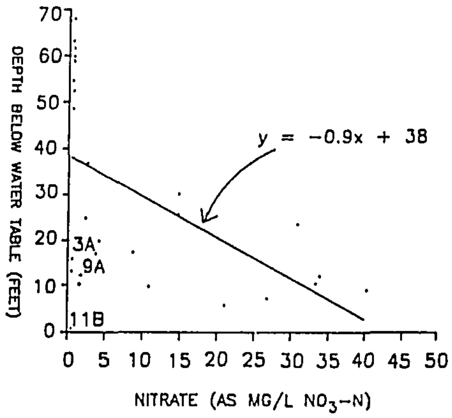


Figure 21. Nitrate Concentrations vs. Depth Below Water Table.

Figure 22 shows a map view of nitrate levels using maximum values from the shallow wells of each well nest. Nitrate values for monitoring wells and residential wells are found in Table 2. High nitrate levels for shallow wells (>10 mg/L NO_3-N) are evident throughout the central and eastern areas except for an undefined area downgradient of the wetland area located southeast of well nest 1. As stated earlier, the redox conditions of the water flowing out of this wetland result in low nitrate and sulfate concentrations in the downgradient wells. Extrapolating flow lines from well nest 11 to well nest 9 shows a possible explanation for the low nitrate levels in wells 9A and 9B, although flow path length from upgradient impacted areas to nest 9 is the most likely explanation.

Relatively low values for nitrate are observed in the western area (well nests 3,6, and 7) although these nests are located directly downgradient from cropland. Chemical data do not indicate a reducing environment in the shallow aquifer region in the western area; therefore, reduced nitrate levels are a result of either lower infiltration of surface contaminants, lower application rates of fertilizer, or both.

Nitrate concentrations decrease slightly from shallow to intermediate well depths and even increase in well nest 4 as seen in Fig. 23. Nitrate levels drop sharply from intermediate to deep wells due to ground-water flow

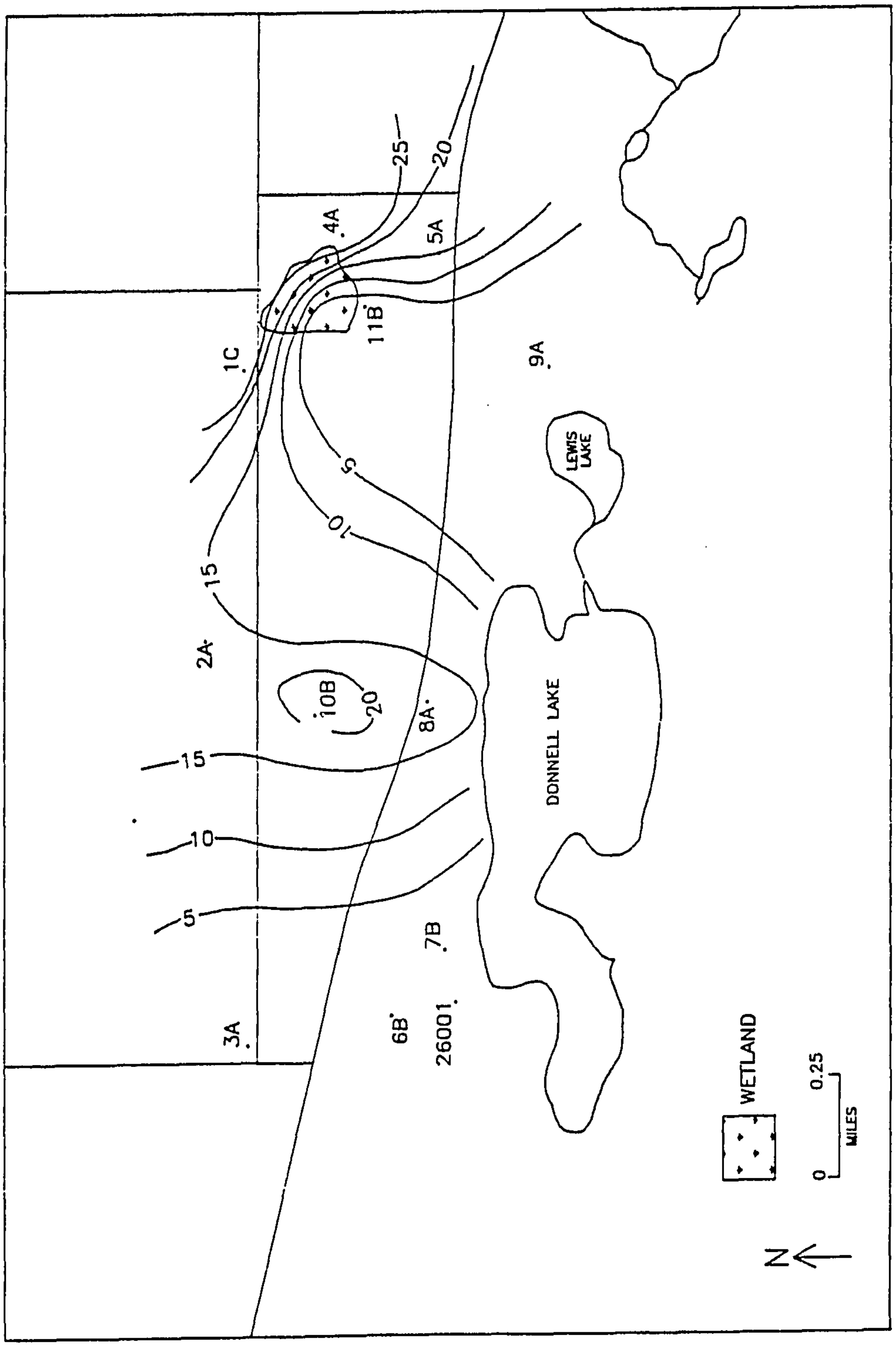


Figure 22. Map View of Nitrate Concentrations (as mg/L NO_3-N) for Shallow Wells.

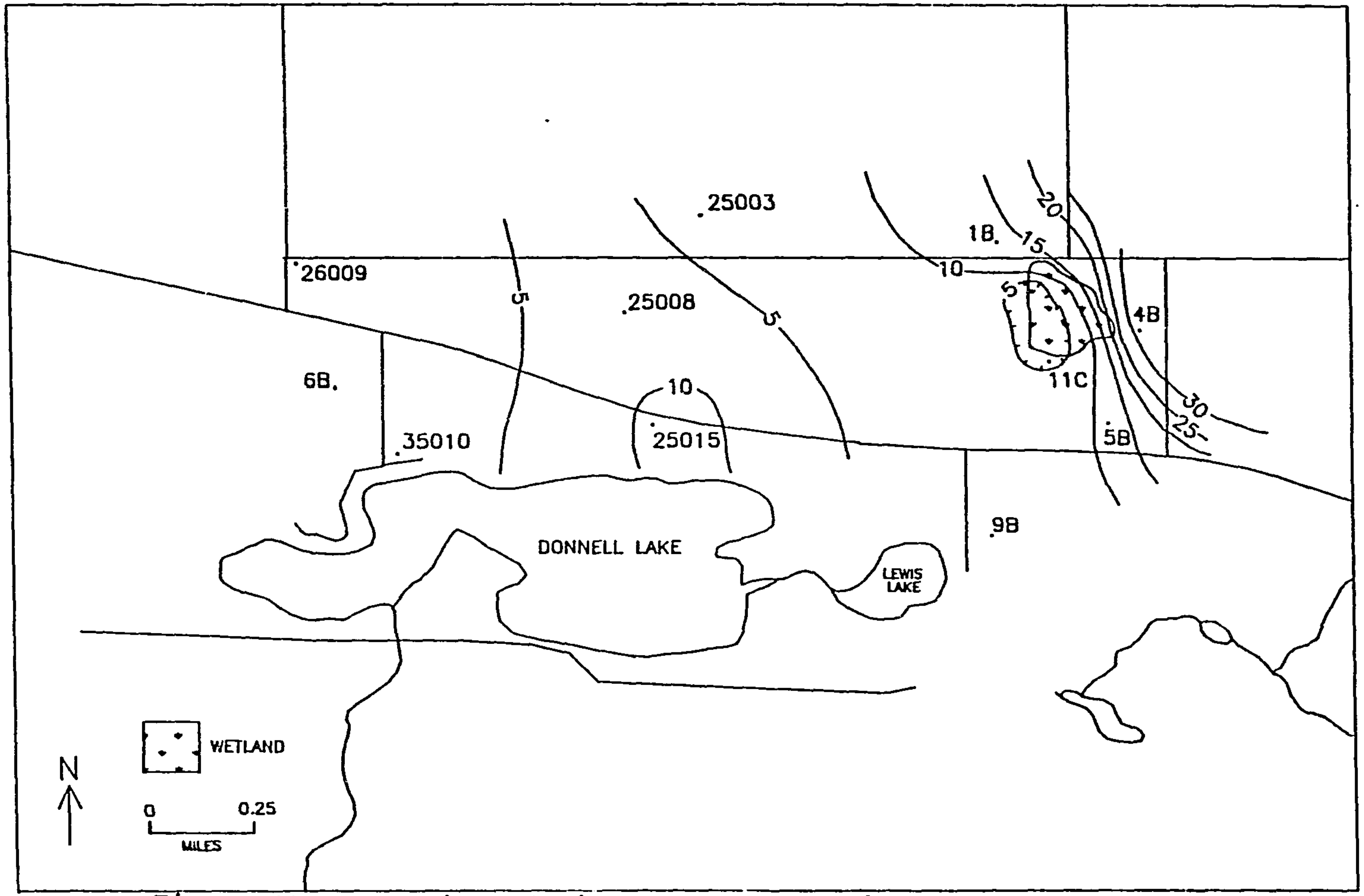


Figure 23. Map View of Nitrate Concentrations (as mg/L NO_3-N) for Intermediate Wells.

patterns and stratigraphy. Many of the deep wells are screened below till which has relatively low permeability and typically retards ground-water flow and contaminant advection. Flow patterns within the saturated zone will determine the vertical distribution of infiltrating contaminants with recharge flow advecting contaminants deeper into the aquifer and transitional or discharging flow retaining contaminants in shallower aquifer regions. Isoconcentration cross sections were constructed to observe the influence of both till stratigraphy and ground-water flow patterns on the vertical and lateral distribution of nitrates.

Figure 24 shows till and clay layers in cross section 3-7 as well as nitrate concentrations. Nitrate values for shallow, intermediate, and deep wells are generally low throughout the area, although the residential wells, 35010 and 35011, show elevated concentrations. Both of these wells are screened above the lower till layer, but are located in a highly discharging area of the shallow aquifer as shown by the equipotential lines. The discharging flow pattern would tend to keep surficial contaminants from penetrating to the depths of wells 35010 and 35011. The explanation for high nitrates in these residential wells may be that flow upgradient is much more recharging than head values of nest 6 indicate.

Figure 25 shows till and clay layers as well as

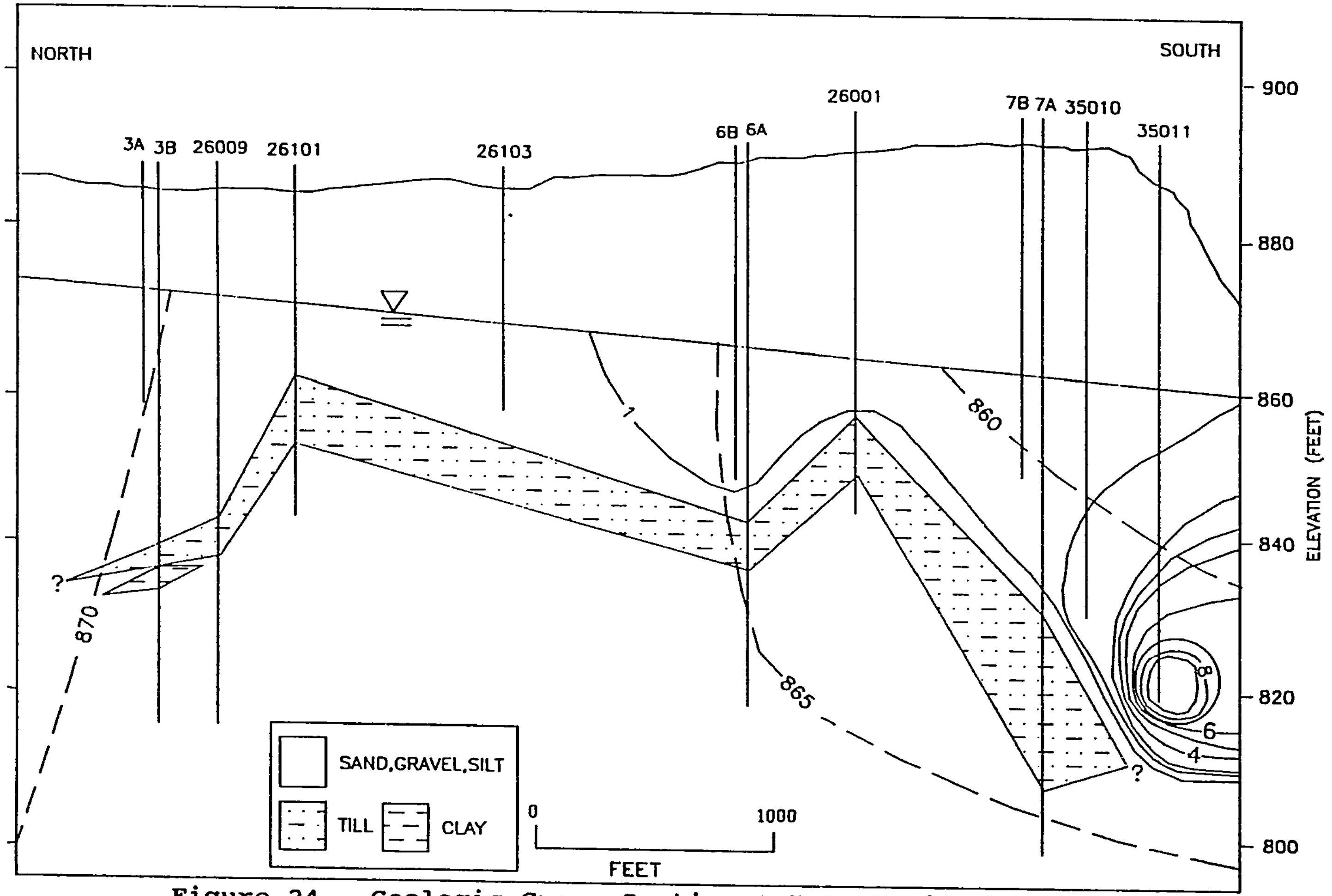


Figure 24. Geologic Cross Section 3-7 Including Nitrate Concentrations in mg/L NO_3-N.

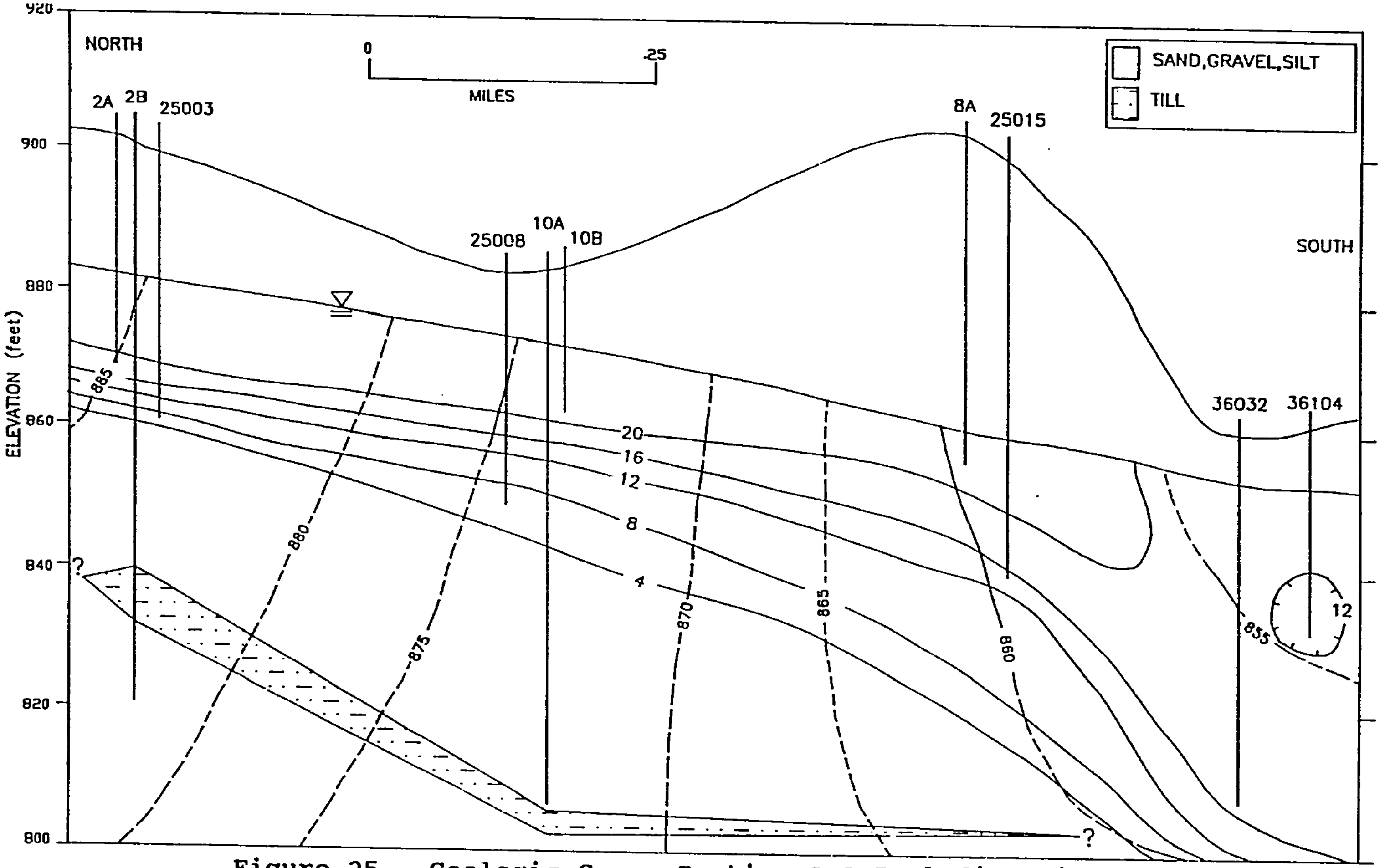


Figure 25. Geologic Cross Section 2-8 Including Nitrate Concentrations in mg/L NO_3-N.

nitrate concentrations for cross section 2-8. The continuous till layer appears relatively lower than in cross section 3-7. The considerable impact of nitrates is observed throughout the cross-sectional area. Ground-water flow is slightly recharging in the north, nearly lateral through the center, and becomes discharging towards the north edge of Donnell Lake. The till layer is deep enough to allow large vertical distribution of nitrates, but a slight vertical gradient confines nitrates to relatively shallow zones.

Figure 26 shows till and clay layers as well as nitrate concentrations for cross section 1-9. The lower till layer is found to the east and west of well nest 1 and 9 and can be assumed to be present below these nests. A strong downward flow component is seen in the north changing to predominantly lateral flow near well nest 9. Nitrate concentrations show the effects of the till as well as flow patterns. Nitrates are advected almost directly downward near nests 1 and 4 and are retarded by the top of the till layer as shown by the non-detect readings in well 30005. Nest 11 shows flow becoming more transitional; however, reduced ground water discharging directly to wells 11B and 11C from the upgradient wetland has non-detect nitrate levels. Wells 5A, 5B, as well as residential wells 30011 and 30007 show elevated nitrate levels. Lack of till barriers coupled with recharging flow facilitates nitrate

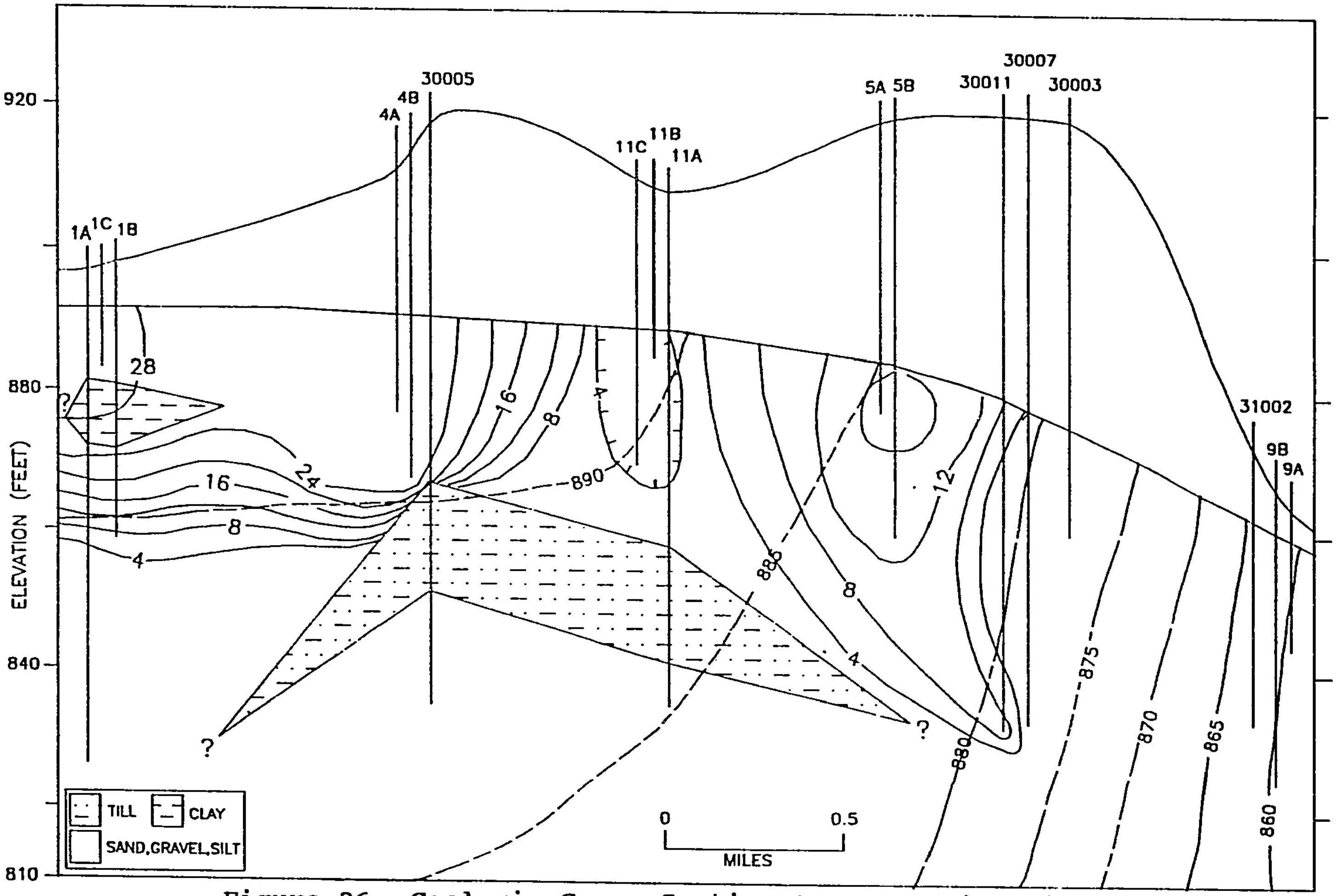


Figure 26. Geologic Cross Section 1-9 Including Nitrate Concentrations in mg/L NO_3-N.

transport to these relatively deep wells. Well nest 9, which includes well 31002, has low or non-detect nitrate levels due to flow path length and lack of surficial input between nest 5 and nest 9. Chemical characteristics of ground water typically become more reducing with path length, and this is seen in nest 9 with elevated iron and ammonium and low dissolved oxygen, nitrate, and sulfate.

Figures 27 and 28 show east-west cross sections of till and clay layers as well as nitrate concentrations roughly perpendicular to ground-water flow. These cross sections complement the north-south cross sections and show more clearly the differences in nitrogen input between the eastern, central, and western areas of the study site. The isoconcentration patterns are consistent with the factors limiting vertical distribution of nitrates as in the other cross sections.

The high concentrations of nitrate in the shallow wells correlate with high potassium and calcium. This correlation is related to the composition of fertilizers and other applied surface materials. Correlation between calcium, potassium, and nitrate is common in the shallow aquifers within agriculturally dominated areas in the neighboring counties of Van Buren and Kalamazoo (Cummings, 1984). Potassium is essential to plant growth, as is nitrogen, and is applied to soil in several different compositional forms such as potassium chloride, potassium

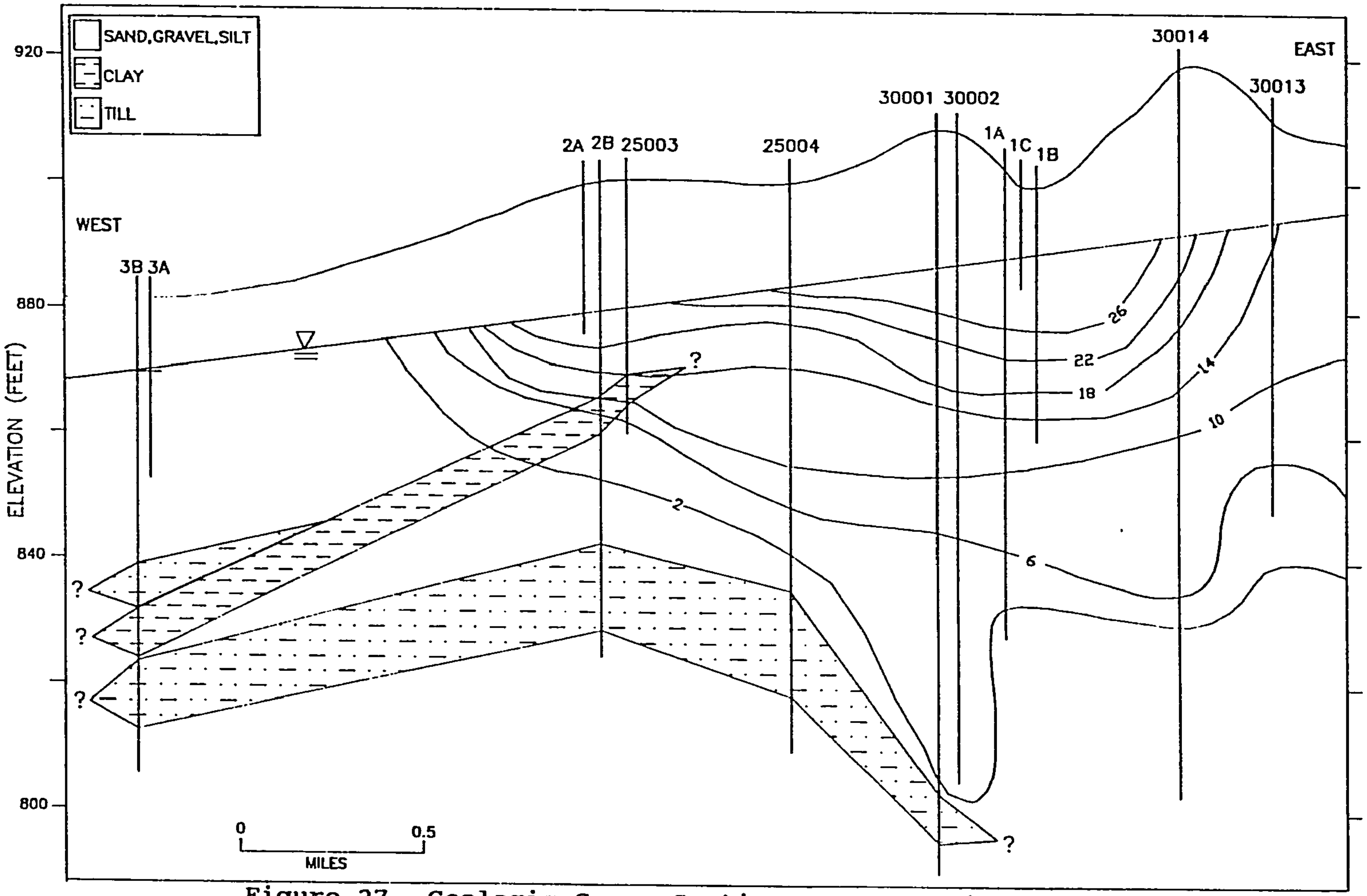


Figure 27. Geologic Cross Section 3-1 Including Nitrate Concentrations in mg/L NO_3-N.

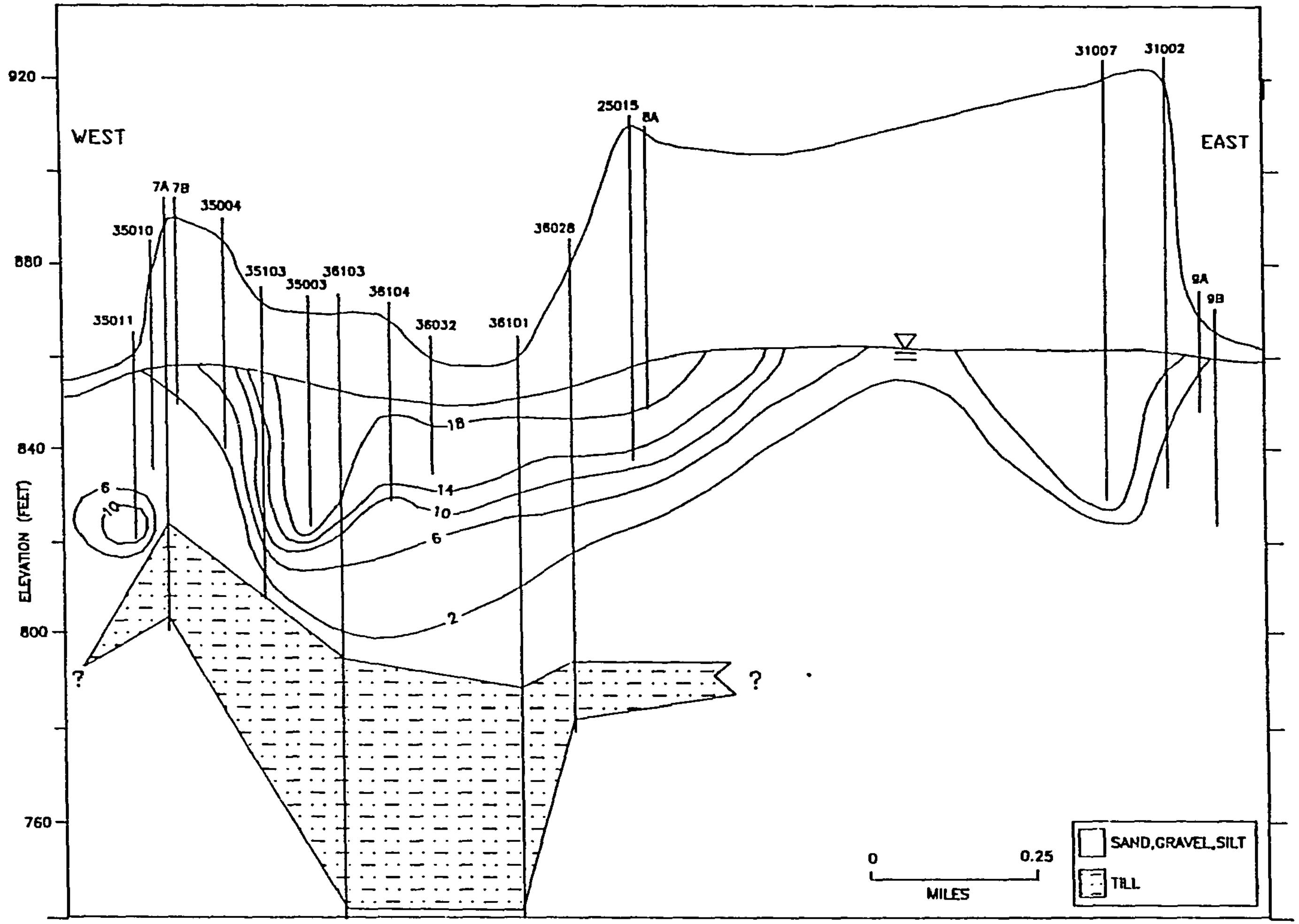


Figure 28. Geologic Cross Section 7-9 Including Nitrate Concentrations in mg/L NO_3-N.

nitrate, and potassium sulfate. The correlation of potassium, nitrate, and chloride indicates use of potassium chloride on crops in addition to a nitrogen fertilizer. Differentiating between chloride from fertilizers and road salt is difficult although correlating chloride concentrations to increases in sodium and potassium levels show a mix of sources. High sodium levels coupled with high chloride concentrations would indicate road salt as the source. High potassium levels correlating with high chloride concentrations would indicate fertilizer as the source of chloride.

The correlation of nitrate and calcium results from the surface treatment of soil with calcium carbonate to reduce acidity (Ervin, 1992). Calcium concentration spikes are seen in wells with nitrate levels greater than 20 mg/L NO_3-N.

The high nitrate-potassium-calcium chemical signature is seen areally in the central and eastern well nests mainly in the shallow wells. Well 4A is the only shallow well in the central-eastern area that does not display high potassium and calcium levels accompanying a high nitrate level. The high nitrate level in 4A may be solely the result of runoff and infiltration of pig waste from adjacent semi-confinement and open swine holdings.

The major reason for the vertical decrease in TDS with depth is the decreasing concentrations of the associated chemical groups (K-Ca-NO_3, Na-Cl) and the decrease in bicarbonate which can be also be linked to the general degradation of shallow ground water (bicarbonate is evolved from soil bacteria processes and indirectly from dissociation of calcium carbonate). From shallow to intermediate depths, the concentrations of potassium, calcium, and sodium decrease sharply while nitrate and chloride levels remain relatively high. Figures 29-32 show the concentration changes of calcium and potassium from shallow to intermediate well depths. Decreases in potassium and calcium from shallow to intermediate wells are largest in the east and central zones where fertilizer impacts were the greatest. The sharp decrease in cations with depth relative to anions is due to greater mobility of the anionic species within leachate because of immobilization of cations by ion exchange in clays as well as organic residue complexation.

Pesticide Analysis

Ground-water samples were screened for herbicides by the Michigan Department of Health through MSU. Results for WMU monitoring and associated residential wells are shown in Table 4. Because the lowest standard used was 0.1 micrograms/L, concentrations lesser or equal to 0.1 micrograms/L can be considered non-detect. Due to variability of the screening process, concentrations between

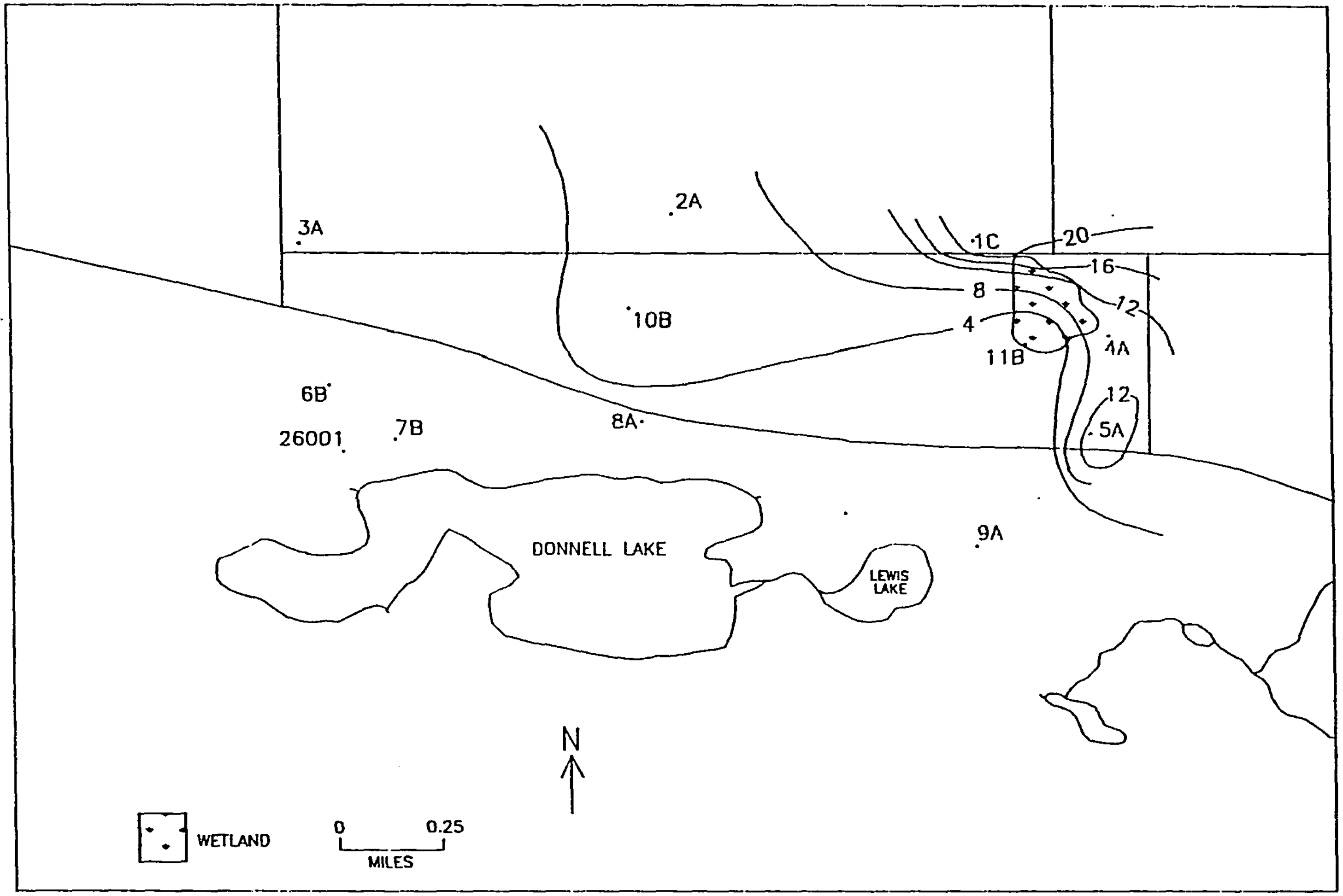


Figure 29. Map View of Potassium Concentrations in mg/L for Shallow Wells.

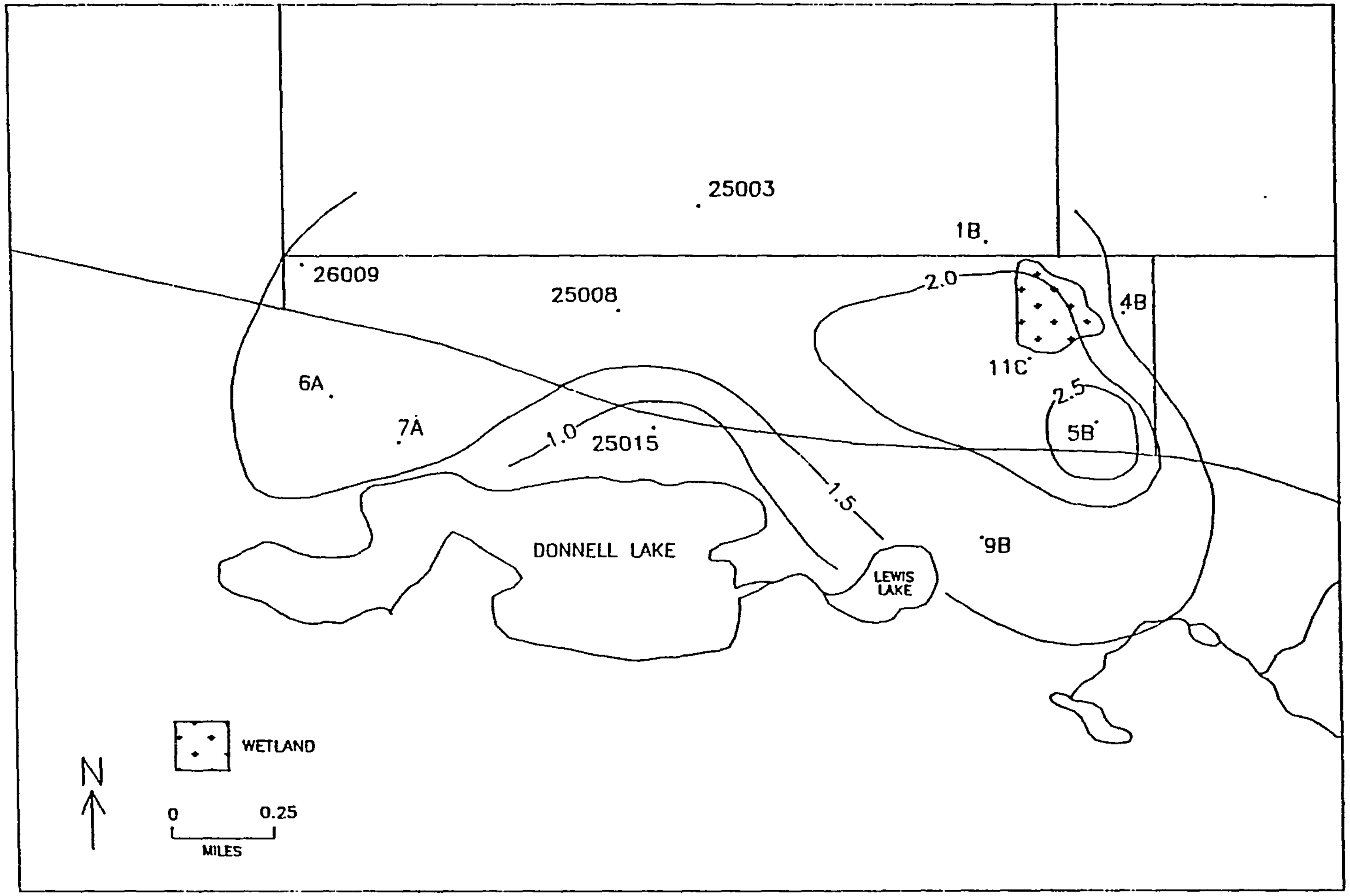


Figure 30. Map View of Potassium Concentrations in mg/L for Intermediate Wells.

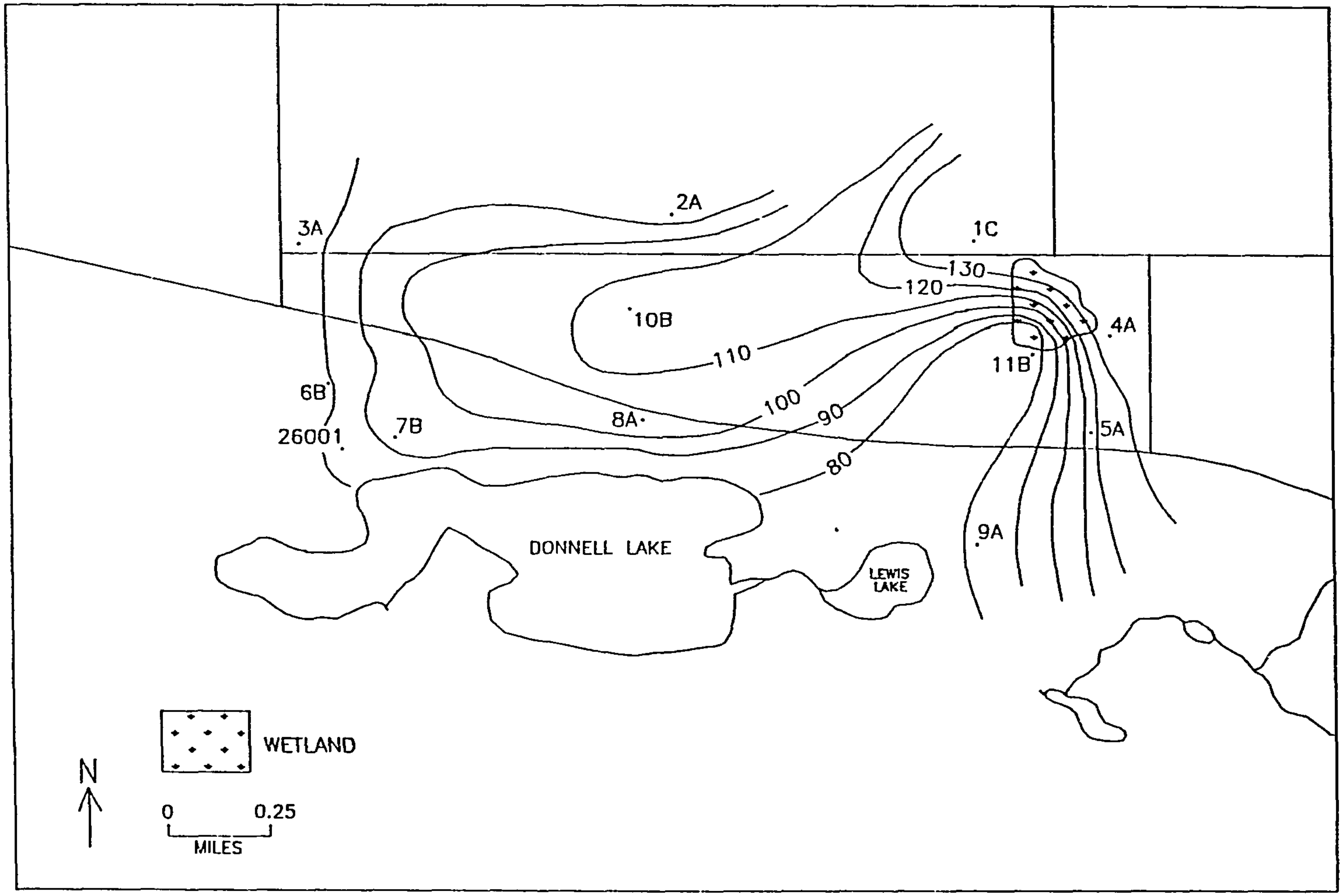


Figure 31. Map View of Calcium Concentrations in mg/L for Shallow Wells.

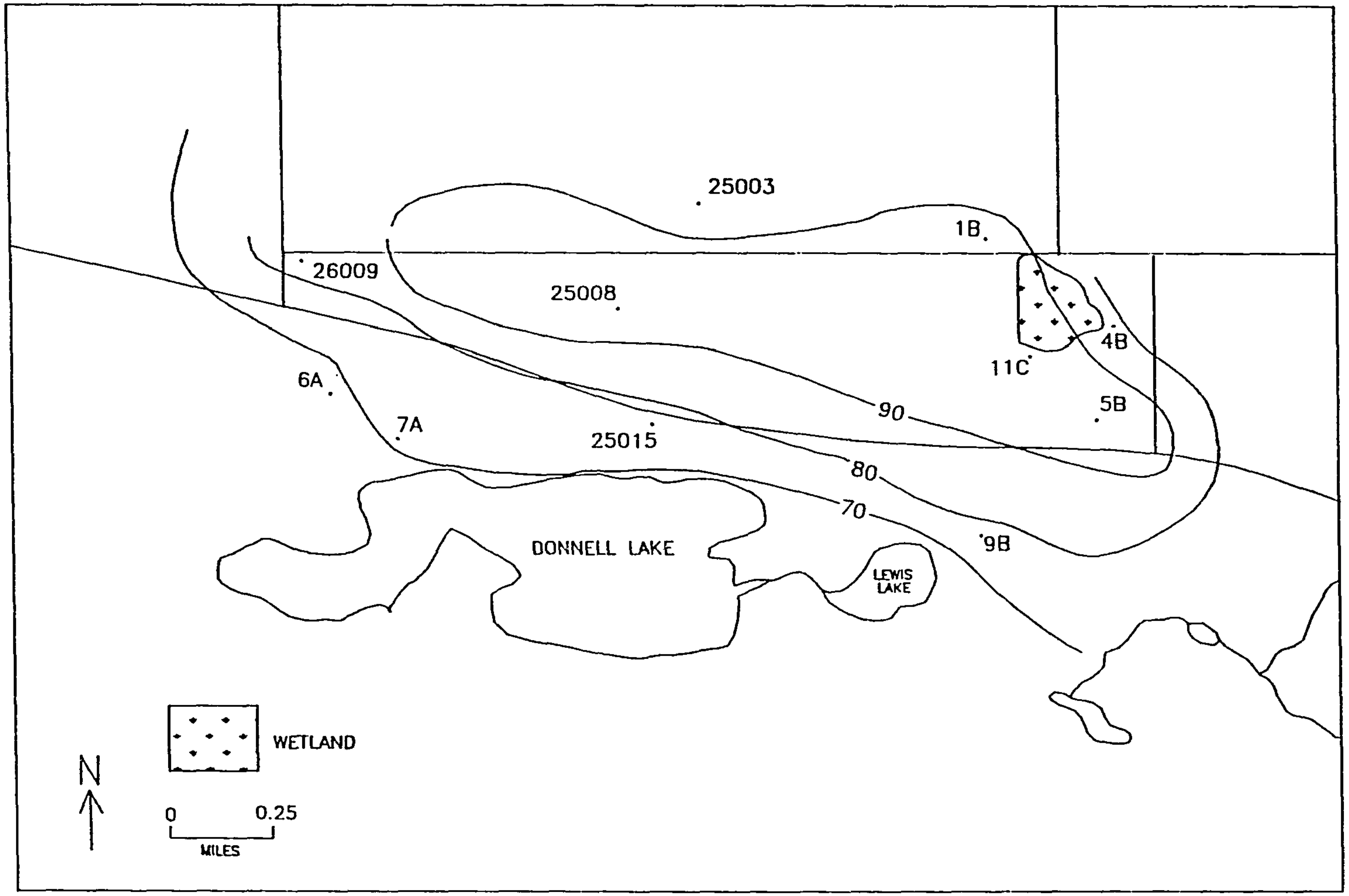


Figure 32. Map View of Calcium Concentrations in mg/L for Intermediate Wells.

Table 4

Pesticide Analysis Results

Well	Depth (feet)*	Atrazine (micrograms/l)	Alachlor (micrograms/l)
1A	62	0.10	0.04
1B	30	0.02	0.06
1C	9	0.19	0.05
25003	20	0.08	0.03
2A	10	1.08	0.03
2B	59	0.07	0.02
26009	53	0.06	0.08
3A	16	0.13	0.10
3B	60	0.08	0.02
30005	55	0.07	0.02
4A	13	0.06	0.04
4B	23	0.17	0.05
5A	6	0.49	0.13
5B	26	0.03	0.03
26001	17	0.13	0.05
6A	49	0.68	0.04
6B	11	0.42	0.04
35010	37	0.07	0.04
7A	69	0.06	0.02
7B	12	0.14	0.13
25015	25	NA	NA
8A	8	0.03	0.03
31002	30	NA	NA
9A	14	0.02	0.02
9B	37	0.03	0.04
10A	64	0.03	0.02
10B	11	0.08	0.03
25008	18	0.02	0.02
11A	50	0.03	0.02
11B	1	0.04	0.05
11C	21	0.04	0.03

NA = no data available
* depth below static water table

0.1-0.15 micrograms/L are considered possible positive detections, and values greater than 0.15 micrograms/L are considered probable positive detections.

With these considerations, most well samples show non-detect herbicide levels for both Atrazine and Alachlor.

Only the shallow wells at nests 3, 5, and 7 show possible detections of Alachlor, and none show probable detections.

Shallow wells at nests 1, 2, 3, 5, 6, and 7 show possible or probable Atrazine detection with wells 5A and 6B showing relatively high levels. Two intermediate wells, 4B and 26001, show Atrazine levels near the cutoff between possible and probable. Two deep wells, 1A and 6A, show Atrazine levels of 0.10 and 0.68 micrograms/L, respectively. Atrazine detection in these deep wells (though only a possible detection in 1A) is unexpected with both wells screened below till layers and showing no other signs of surface contaminant influence. The presence of Atrazine at these depths may indicate discontinuities in the till layers or inability of the till layers to retard herbicide transport.

Mineral Saturation Analysis

Mineral saturation indices were calculated using WATEQF (Plummer, 1976). Table 5 shows the saturation indices with respect to individual minerals. Quartz is

Table 5

Mineral Saturation Data for Ground-Water Samples

	Log IAP/K				
Well	Quartz	Calcite	Dolomite	Cristobalite	Chalcedony
1A	.54	.11	-.10	.09	-.01
1B	.66	.17	.06	.21	.11
1C	.61	.10	-.40	.16	.05
2A	.63	.11	-.19	.18	.08
2B	.70	.03	-.29	.25	.15
25003	.60	.15	-.09	.15	.05
3A	.35	-.15	-.61	-.09	-.17
3B	.60	.18	.13	.16	.08
26009	.35	-.06	-.36	-.08	-.16
4A	.62	-.21	-.51	.19	.09
4B	.63	-.12	-.70	.19	.09
30005	.50	-.12	-.59	.05	-.04
5A	.53	.06	-.22	.09	.01
5B	.51	.13	-.03	.07	-.01
6A	.54	.13	.02	.10	.02
6B	.43	.18	.09	-.004	-.09
26001	.39	.01	-.28	-.04	-.13
7A*	.58	.43	.64	.15	.06
7B	.52	.16	-.01	.08	.002
8A	.55	-.10	-.50	.11	.01
9A	.49	.25	.14	.05	-.03
9B*	.54	.31	.34	.11	.03
10A	.51	.16	.08	.06	-.03
10B	.52	.10	-.23	.08	-.02
25008	.53	.19	.11	.09	.006
11A	.63	.20	.05	.19	.09
11B	.49	-.04	-.55	.04	-.05
11C	.59	-.03	-.33	.14	.04

* Wells 9B and 7A are also saturated with Aragonite.

oversaturated in every sample and the other SiO_2 polymorphs, chalcedony and cristobalite, are oversaturated in a majority of the samples. This can be attributed to the concentration of silicic acid created by dissolution of silicate minerals in the aquifer material. Silicic acid is the only factor determining the ion activity product of quartz, cristobalite, and chalcedony, and, subsequently, these minerals are often oversaturated because of the abundance of silicate minerals in glacial sands. Quartz is more often oversaturated because of the greater thermodynamic stability of quartz as compared to chalcedony and cristobalite.

Calcite, aragonite, and dolomite vary in saturation indices depending on chemical and physical characteristics of the ground water. The equilibrium constant for calcite and aragonite is the product of calcium and carbonate activities. The ground water is typically undersaturated with respect to aragonite because of the relatively higher equilibrium constant compared to calcite (calcite is more stable). Although calcium and carbonate activities are of equal importance in determining calcite and aragonite saturation, carbonate activity and especially factors controlling carbonate activity (pH) seem to have greater influence on saturation characteristics. Wells 4B and 8A show high calcium concentrations and yet are unsaturated with respect to calcite and aragonite. In the wells saturated with respect to calcite, calcium activities varied greatly. Ground water with moderate to high carbonate activities shows consistent oversaturation with respect to calcite with low carbonate water showing undersaturation. Carbonate activity is a function of temperature, pH, and alkalinity. Alkalinity is composed mainly of bicarbonate which contributes carbonate by dissociation. High pH values also correspond to higher carbonate concentrations. High pH maintains a relatively higher CO_3/HCO_3 ratio compared to more acidic water. Slight changes in pH may change the character of the water from undersaturated to oversaturated with respect to calcite and aragonite. The pH range of the ground water sampled (7.0 - 7.6) is enough to cause a shift in $CaCO_3$ solubility. Wells 7A and 9B have the highest pH values and are the only two wells oversaturated with respect to aragonite. Temperature affects mineral solubility and equilibrium constants but the small range of temperatures in the ground water sampled has an insignificant influence on carbonate activity. High carbonate activity, which is dependent on pH, is the main influence on saturation characteristics with respect to calcite.

The mineral saturation characteristics of the groundwater samples reflect the lithologic composition of the aquifer material and resulting dissolution. Contamination inputs such as additional calcium and carbonate have little effect evident by the fact that there is no pattern of saturation index change between samples influenced by contamination and those not influenced.

CONCLUSIONS

The ground-water chemistry in the Donnell Lake region indicates contamination from surface processes. Infiltration of applied agricultural constituents, livestock waste, and road salt are the main contributors of several major chemical species in the shallow ground water. Nitrate concentrations exceed the MCL of 10 mg/L NO_3-N in a majority of the shallow monitoring wells (1 to 16 feet below water table) and a few of the intermediate wells (17 to 53 feet below water table). Traces of two herbicides, Alachlor and Atrazine, are found in about half of the shallow wells and also in some intermediate and deep wells.

Characteristic patterns in water chemistry result from different surface inputs. The dominant pattern is a high nitrate-calcium-potassium signature near and downgradient from corn and soybean fields. This signature is a direct result of surface application of fertilizer and lime and subsequent infiltration and leaching into ground water. High sodium-chloride values are a result of runoff and leaching of road salt. A certain amount of chloride is also contributed by fertilizer applications in the form of potassium-chloride or manure.

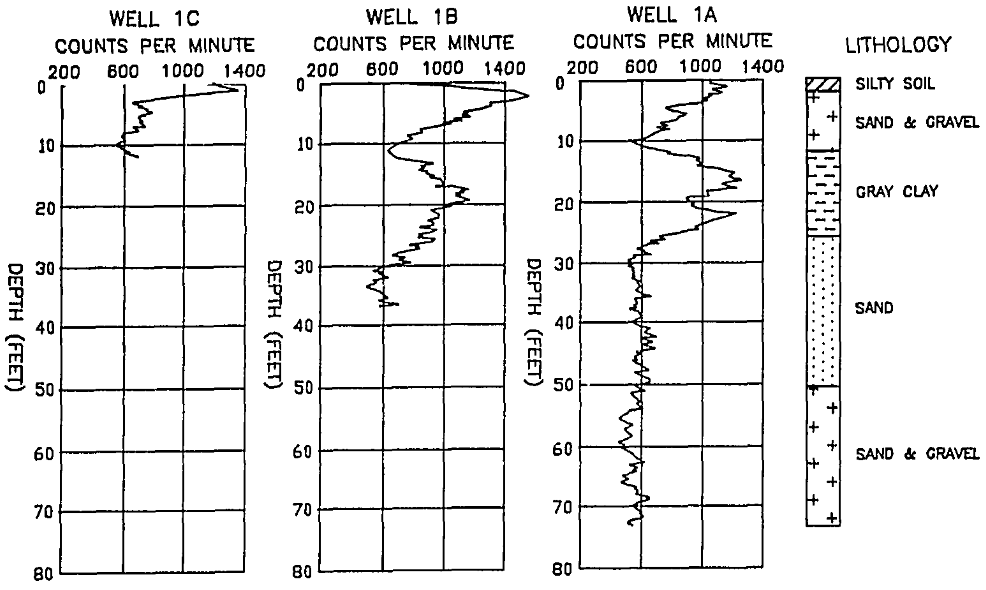
Nitrate is also derived from pig waste. The high density of pigs in the central part of the study area, mainly in open feedlots, creates a large amount of waste very susceptible to surface runoff into surface water bodies and leaching into ground water.

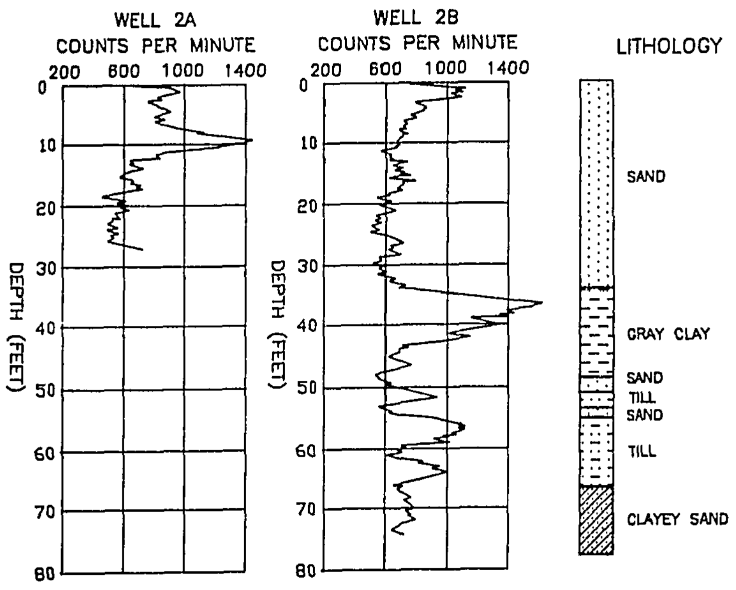
The pattern of high concentrations of certain chemical species is mainly limited to shallow ground water within 15 feet of the static water table. Nitrate and chloride levels stay relatively high to intermediate depths with sharp concentration drops in sodium, potassium, and calcium due to cation exchange and complexation. The deep wells (49 to 69 feet below water table) show a large drop in total dissolved solids due mainly to limited contamination effects are a result of mechanical dispersion of surface infiltration, stratigraphic partitioning due to low permeability layers, and limited recharge flow.

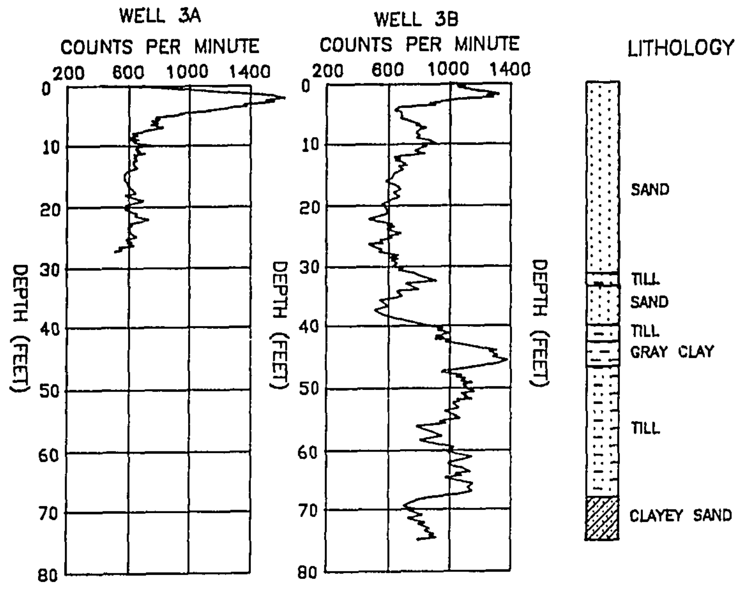
High levels of contamination in shallow ground water are an additional problem for Donnell lake and other nearby surface water bodies. The lakes and streams are fed by overland runoff and shallow ground water. Much of the recharging water is contaminated and increases nutrient loading. This may render the chemistry of the lakes unfit for certain ecosystems and recreational use. No lake samples were analyzed and all monitoring wells and most residential wells are located upgradient of septic tanks surrounding Donnell lake. However, with over 200 cottages (seasonal and permanent residences) surrounding the lake, septic effluent likely adds to shallow ground-water degradation and subsequent discharge into surface water bodies.

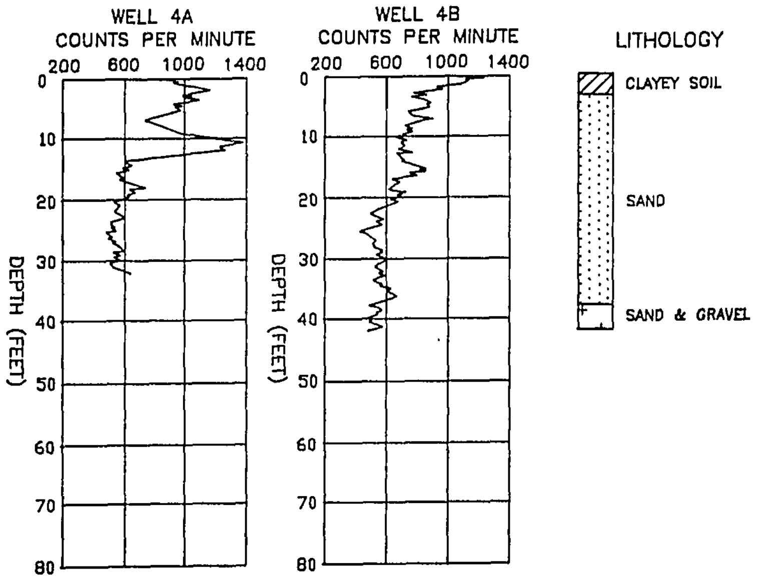
Appendix A

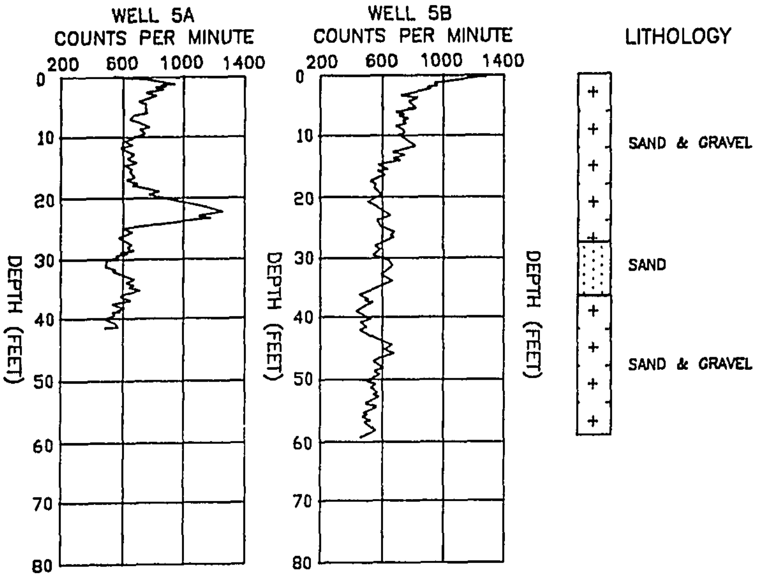
Gamma Ray Logs and Stratigraphic Cross Sections of WMU Monitoring Wells

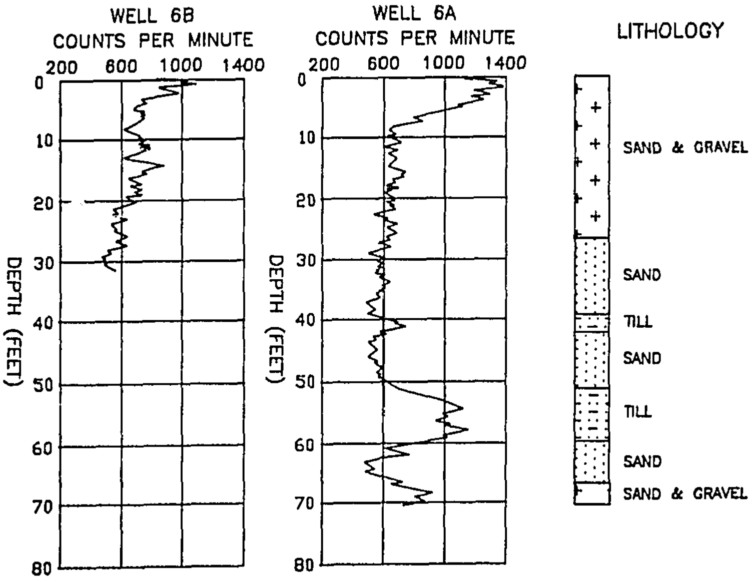

WELL 1C
COUNTS PER MINUTE
WELL 1B
COUNTS PER MINUTE
WELL 1A
COUNTS PER MINUTE
200 600 1000 1400
DEPTH (FEET)
0 10 20 30 40 50 60 70 80
LITHOLOGY
SILTY SOIL
SAND & GRAVEL
GRAY CLAY
SAND
SAND & GRAVEL

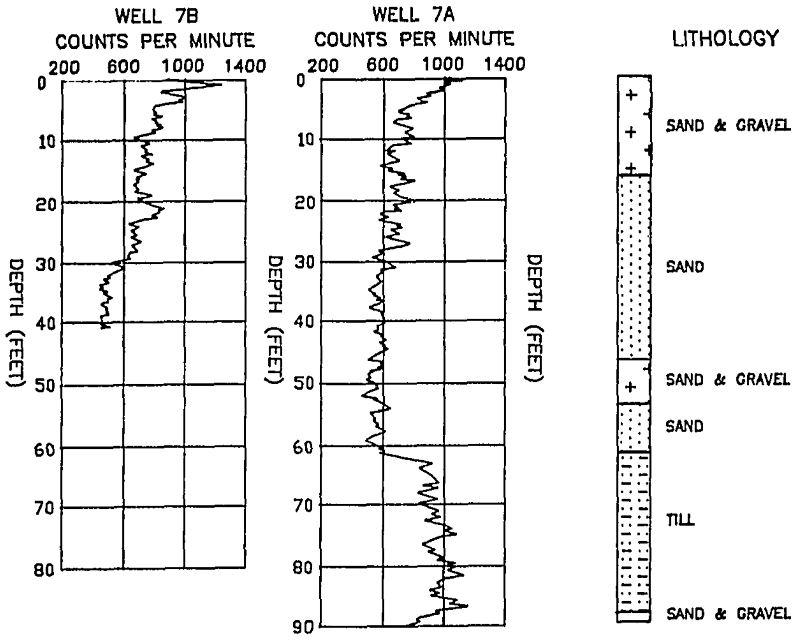

WELL 2A
COUNTS PER MINUTE
WELL 2B
COUNTS PER MINUTE
200 600 1000 1400
DEPTH (FEET)
0 10 20 30 40 50 60 70 80
LITHOLOGY
SAND
GRAY CLAY
SAND
TILL
SAND
TILL
CLAYEY SAND

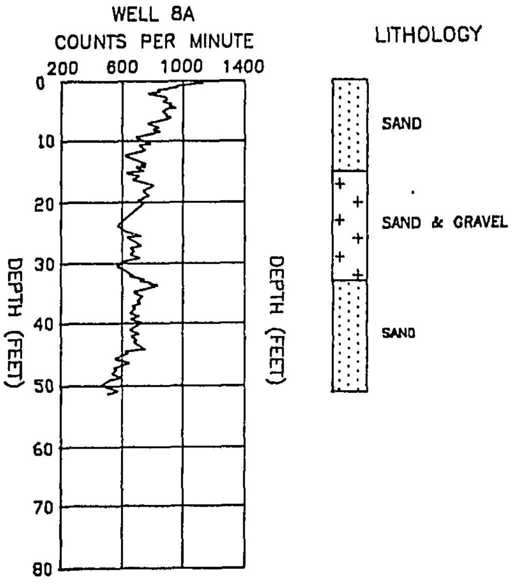

WELL 3A
COUNTS PER MINUTE
200 600 1000 1400
WELL 3B
COUNTS PER MINUTE
200 600 1000 1400
DEPTH (FEET)
0 10 20 30 40 50 60 70 80
LITHOLOGY
SAND
TILL
SAND
TILL
GRAY CLAY
TILL
CLAYEY SAND

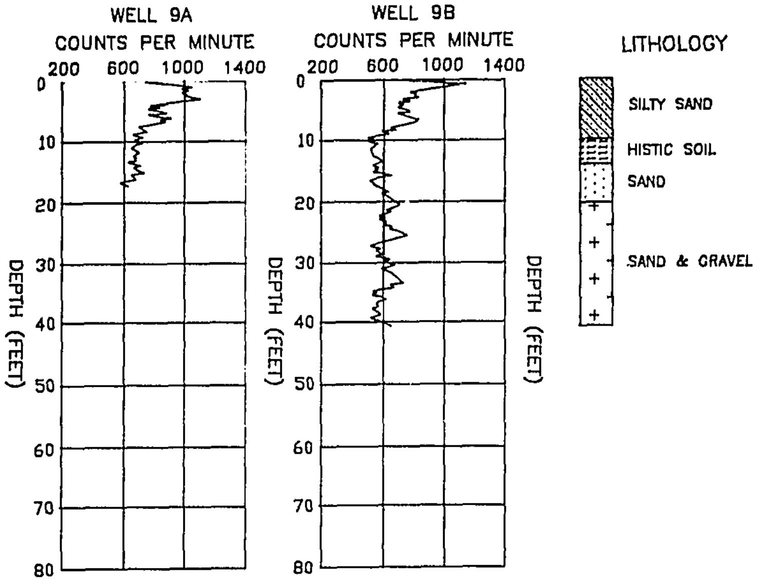

WELL 4A
COUNTS PER MINUTE
200 600 1000 1400
WELL 4B
COUNTS PER MINUTE
200 600 1000 1400
DEPTH (FEET)
0 10 20 30 40 50 60 70 80
LITHOLOGY
CLAYEY SOIL
SAND
SAND & GRAVEL

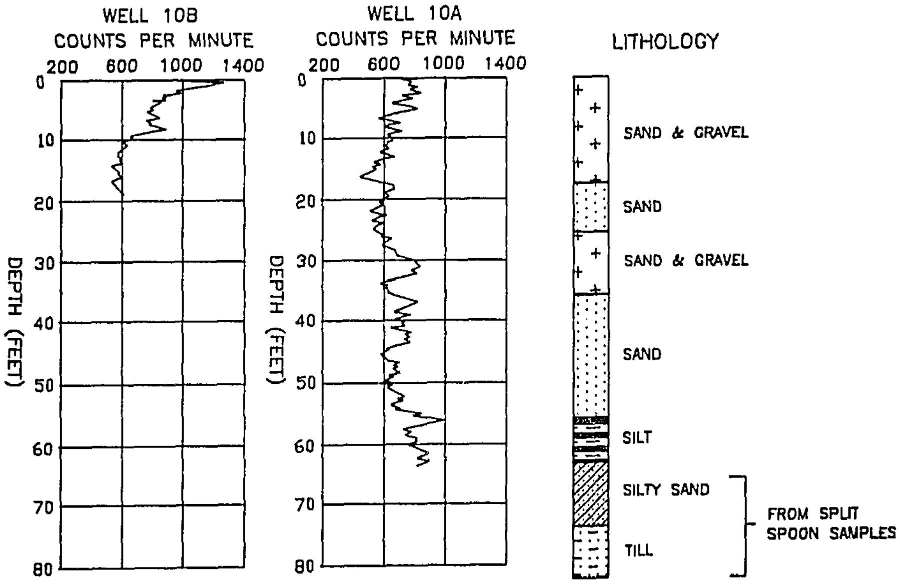

WELL 5A
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
DEPTH (FEET)
WELL 5B
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
DEPTH (FEET)
DEPTH (FEET)
LITHOLOGY
SAND & GRAVEL
SAND
SAND & GRAVEL


WELL 6B
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
DEPTH (FEET)
WELL 6A
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
DEPTH (FEET)
LITHOLOGY
SAND & GRAVEL
SAND
TILL
SAND
TILL
SAND
SAND & GRAVEL


WELL 7B
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
DEPTH (FEET)
WELL 7A
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
90
DEPTH (FEET)
DEPTH (FEET)
LITHOLOGY
SAND & GRAVEL
SAND
SAND & GRAVEL
SAND
TILL
SAND & GRAVEL


WELL 8A
COUNTS PER MINUTE
200 600 1000 1400
0
10
20
30
40
50
60
70
80
DEPTH (FEET)
DEPTH (FEET)
LITHOLOGY
SAND
SAND & GRAVEL
SAND


WELL 9A
COUNTS PER MINUTE
200 600 1000 1400
WELL 9B
COUNTS PER MINUTE
200 600 1000 1400
DEPTH (FEET)
0
10
20
30
40
50
60
70
80
LITHOLOGY
SILTY SAND
HISTIC SOIL
SAND
SAND & GRAVEL


WELL 10B
COUNTS PER MINUTE
200 600 1000 1400
WELL 10A
COUNTS PER MINUTE
200 600 1000 1400
DEPTH (FEET)
0
10
20
30
40
50
60
70
80
LITHOLOGY
SAND & GRAVEL
SAND
SAND & GRAVEL
SAND
SILT
SILTY SAND
TILL
FROM SPLIT SPOON SAMPLES

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