Evaluation of Nitrate Contamination and Dissipation Trends in the Englevale Aquifer, Ransom and Sargent Counties, ND: 1996-2006

By
W. M. Schuh

Water Resources Investigation No. 46
North Dakota State Water Commission

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The author is solely responsible for the analysis and conclusions presented in this report. Thanks to Royce Cline of the North Dakota State Water Commission (SWC) who first identified and defined the problem analyzed in this report, and who designed and supervised the monitoring-well network and sampling plan used. Thanks to Mr. Cline also for valuable corrections and insights in review of this manuscript. Thanks also to Merlyn Skaley of the SWC for many hours of dedicated field sampling in this project, and to Brenda Hove of the SWC for assistance in review and preparation of this report.

EXECUTIVE SUMMARY

Nitrate analyses of water samples collected from irrigation wells by the North Dakota State Water Commission (SWC) in 1996 indicated the presence of elevated nitrate concentrations. To better define the extent, significance, sources and causes of increasing nitrate, the North Dakota State Water Commission augmented or constructed stratified monitoring well nests at several locations in the aquifer during 1996 and 1997. The wells were then sampled seasonally in 1997 and 1998, and annually in the fall of 1999 through 2006. Irrigation wells (as many as 42 wells) were sampled annually from 1996 through 2001.

- Nitrate was constrained and stratified within the upper 10 to 20 feet of the aquifer.

- Metrics used to evaluate the spatial distribution of nitrate contamination were: (1) total "nitrate-N load," and (2) Potential Mixed Concentration Index (PMCI) for each well site and each sample date. The purpose of the nitrate-N load parameter was to provide a single quantitative and site-specific metric for each date and site for comparative analysis, and for comparison with fertilizer applications rates. Nitrate-N load was calculated by integrating nitrate concentrations over the sampled depth and converting to units of lb./ac. for equivalency with fertilizer applications.

- The purpose of the PMCI was to provide an index for comparing stratified nitrate distributions with toxicological standards, by approximating the equivalent concentration for a fully mixed vertical column. PMCI (in mg/L) were calculated by dividing the total nitrate-N by the saturated thickness of the aquifer. For irrigation wells, the mixed concentration (labeled MCI) for the well as sampled was used for comparison.

- Because well nests were not completed until 1997, and previous water samples were collected almost entirely from wells screened near the bottom of the aquifer, the best well set for evaluating the time of transition from lower to higher nitrate-N loads is the irrigation well set. Because the irrigation well samples were collected only through 2001, the observation well set provides the best indicator of the fate of nitrogen after 1996.

A substantial increase in nitrate-N load occurred in the Englevale aquifer, likely in the early to mid 1990s.

- A substantial increase in nitrate-N load occurred at some time between 1990 and 1996. A comparison of composite statistics for all irrigation well water samples collected between 1975 and 1995, and those collected between 1996 and 2001 indicated that the median nitrate-N load approximately tripled from 0.23 lb./ac. (106 samples) to 0.59 lb./ac. (108 samples).

- Prior to 1996, all but one water sample collected from irrigation wells had mixed concentrations below 3 mg/L nitrate-N, and one sample was between 5 and 10 mg/L. From 1996 through 2001, 65% were less than 3 mg/L, 80% were less than 5 mg/L (15% between 3 and 5 mg/L), and 96% were below 10 mg/L (4% of the samples tested at above 10 mg/L nitrate-N.

- During and after 1996 median PMCI for observation well sites were distributed as 51% below 3 mg/L and 78% below 10 mg/L. None were between 3 and 5 mg/L, 27% were between 5 and 10 mg/L, and 22% were above 10 mg/L.

- Nitrate-N loads were generally lower for irrigation wells than for observation well nests. Differences were likely caused by: (1) Larger spatial representation in irrigation well samples, which would dampen local extremes; (2) sample bias, with monitoring wells placed preferentially in areas likely to be of contaminant concern, or indicated to be so by nearby irrigation well samples; (3) extraction of nitrate near irrigation wells through pumpage; and (4) some of the irrigation wells are screened in the lower unit(s) of the Englevale aquifer.

The primary cause of nitrate-N loading was climate-driven.

- For the observation wells, highest mean and median nitrate concentrations and loads for each sample date occurred early, usually at the beginning (1996-1997) of the sample period, and declined steadily through 2006. A likely cause of initial elevated nitrate was the wet climatic shift which began in 1993. A strong upward shift in seasonal (winter) precipitation occurred beginning in 1993. Shallow nitrate data from observation wells was too sparse before 1996 to substantiate the time during which flushing occurred. Irrigation well samples, however, indicated that the nitrate contaminant event(s) likely occurred between 1991 and 1996. During that time period, enhanced nitrate loading may have occurred abruptly following a few large events, or gradually as a general response to the climate shift. A second minor nitrate peak in some wells in 1997 was likely caused by recharge from the exceptionally wet spring of that year. Similar elevated nitrate loads were identified for other aquifers, including the Karlsruhe aquifer in McHenry County, and the Carrington aquifer, a shallow confined aquifer in Foster County. Nitrate in the Carrington aquifer increased quickly following 1993, and then began to decline. The Karlsruhe aquifer had undergone loading to the extent of four million pounds of nitrate-N by 2000. The exact time of Karlsruhe loading is unknown. Generally, it appears that the Englevale aquifer, and several other aquifers in North Dakota experienced large flushes of nitrate during the 1990s in response to wetter climate, and large precipitation events.

- Median and mean nitrate-N loads from water samples collected from observation wells in the Englevale aquifer were most strongly correlated with (1) five-year moving average and annual winter precipitation (P), and (2) five-year moving average, and annual total P. Nitrate contamination events thus corresponded to periods of high recharge and subsequent leaching. Periods of nitrate dissipation corresponded to periods of lower P and declining water tables.

- Median and mean nitrate-N loads were inversely correlated with a temperature-based estimate of Penman-Monteith potential-evapotranspiration (PET). PET may serve as an indirect inverse indicator of P through greater cloud cover and lower temperatures associated with low PET because of a greater proportion of latent to temperature-measurable heat caused by evaporation of greater P.

There was no correlation between irrigation water use and nitrate-N loads.

- The strong correlation with enhanced winter P and the inverse correlation with PET support the hypothesis of a climatic cause.

Most well sites are improving.

- During and following 1996 the predominant nitrate loading trend was decreasing. The rate of nitrate-N load dissipation was approximately 4% per year for the mean, and 8% per year for the median. This compares with dissipation rates of 6% per year measured from 2000 through 2006 in the Karlsruhe aquifer.

- The original irrigation wells in which high nitrate concentrations were first observed in 1996 in the southern portion of the study area (irrigation well 133-057-31DCB). This well was screened in a confined unit of the eastern channel of the Englevale aquifer. Nitrate detected in this well, and other nearby wells, was likely transported to the lower aquifer unit through connections with the shallow surficial aquifer unit, or through connections formed with the shallower aquifer unit during periods of exceptionally high water table following 1993. The nitrate could have moved a considerable distance in a short period through the gravelly aquifer materials. Peak concentrations in irrigation well 133-057-31DCB, and others screened in the same unit farther south in Section 132-058-01, exhibited peak nitrate concentrations in 1996 and 1997, and then recovered fully to negligible concentrations by 2001.

The primary cause of nitrate dissipation from the Englevale aquifer is denitrification.

- Nitrogen (^{15}N) and oxygen (^{18}O) isotopes indicate that denitrification is a cause of nitrate dissipation in the Englevale aquifer. Isotopes were determined for nitrate in stratified water samples from the north, middle and southern portions of the aquifer. Isotopic signatures for nitrate ^{15}N and ^{18}O in the shallow oxidized zone are consistent with a nitrified ammonium or urea source. Both nitrate ^{15}N and ^{18}O in nitrate increase with depth, indicating dissipation of nitrate with depth through denitrification. The depth distribution of both isotopes is similar for all sites, and can be described using composite exponential functions. The similarity suggests a similarity of recharge and hydrologic controls on solute redistribution between the measured sites.

- Sulfate sulfur isotopes (^{34}S) are consistent with, but not exclusive to autotrophic denitrification using mineral sulfur (possibly pyrite) as an electron donor.

- The majority of observation well sites exhibit inverse stratification of nitrate and sulfate in the upper 10 to 20 feet of the aquifer, indicating likely autotrophic denitrification. For several sites the inverse regression coefficient is within a reasonable range for approximation of the stoichiometric expectation (1.62) for autotrophic denitrification using pyrite iron and sulfur as electron donors.

- Dissolved oxygen below the surficial oxidized zone, remained low and quickly returned to low values after oxygenation with recharge waters. This means that the surficial oxidized zone is likely depleted of reducing minerals through previous long-term oxidizing events, and the unoxidized zone is likely maintained and controlled by the persistence of reducing minerals.

- Declining water tables may have enhanced nitrate dissipation. Because of mineral controls on the reducing environment, the correlation between decreasing nitrate loads and decreasing precipitation and water levels may be partially caused by constriction of the oxidizing zone. Concentration of leached nitrate in closer proximity to the electron donors may be a major mechanism for nitrate dissipation. Conversely, if this is true we may expect increasing nitrate loads with increasing water tables and precipitation in the future, not only from increased leaching rates, but from decreased dissipation rates as well.

- Nitrate-N loads in most (73%) of the observation well sites decreased in nitrate from 1996 (1997) through 2006. The largest proportion of well sites with decreasing nitrate was in the middle portion of the aquifer (83%), followed by the northeast (78%), the northwest (64%), and the south (25%). All nitrate loads and concentrations in the south, however, were low throughout the monitoring period.

- Of ten observation well sites having final PMCI above 10 mg/L, seven were improving, and three were exhibiting increasing loads and concentrations.

A second cause of nitrate dissipation may be attributed to changing fertilizer management by area producers.

- A meeting was conducted with SWC, Health Department, and NDSU Cooperative Extension Service representatives and area producers in the spring of 1997 to discuss improvement of nitrate management practices. Most area producers changed application programs to enhance nitrate retention. A lower nitrate influx rate is a necessary and complementary factor for decreasing nitrate loads in the aquifer. Its effects are difficult to measure, but it is reasonably certain that more conservative nitrate management would have a substantial effect in preventing leaching during wet climatic periods.

Most of the aquifer is classified as very low or low with respect to nitrate contamination. Approximately eight sections are identified for remedial attention.

- A classification scheme, consisting of seven classes, was devised for evaluating the nitrate-N load and PMCI with respect to aquifer nitrate management. Classes were: (1) very low (< 3 mg/L, all loads), (2) low (3-5 mg/L, all loads), (3) moderately high (5-10 mg/L, all loads), (4) high, very vulnerable (> 10 mg/L, 0-50 lb./ac.), (5) high, vulnerable (> 10 mg/L, 50-120 lb./ac.), (6) high, somewhat vulnerable (> 10 mg/L, 120-310 lb./ac.), and (7) High Load (> 10 mg/L, > 310 lb./ac.).

- Most of the southern, middle and northwestern portions of the aquifer were very low to low with respect to nitrate contamination. Areas of concern were limited to eight quarter sections. These include (from north to south): 134-057-18B, 134-057-18C, 134-057-30D, 134-058-25C, 134-058-25D, 133-058-25B, 132-058-01C, and 132-058-35A. Most of these are either improving, or fluctuating with respect to nitrate loads. Large nitrate-N in 134-058-25C and -25D may have been affected by point-source contamination, and may warrant ongoing monitoring. These sites, however, have shown substantial improvement over the measurement period.

In summary, nitrate loads increased in the Englevale aquifer during the mid-1990s. Increases were likely caused by more leaching and a thicker aquifer oxidized zone, resulting from wetter climate. Nitrate loads have partially dissipated from most of the aquifer. The main cause of dissipation is denitrification. Dissipation rates appear to be concentration-dependent and decrease at a decreasing rate. Overall, nitrate contamination levels for most of the Englevale aquifer have been very low to low. There are approximately eight quarter sections of concern. Most of the Englevale aquifer has been improving with respect to nitrate loads since 1996. Nitrate conservation management should be routinely practiced over the entire aquifer, and with particular care in the identified areas of concern, and in areas where the aquifer is thin and therefore more vulnerable to nitrate concentration and retention.

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INTRODUCTION

Since 1976 the Englevale aquifer in southeastern North Dakota and northeastern South Dakota has undergone large-scale development of ground-water for irrigation of high-value agricultural crops. At the present time about a third of the lands overlying the aquifer in Ransom County and Township and Range 132-058 of Sargent County, North Dakota, are irrigated (Cline and others 1993).

In 1996, Royce Cline of the North Dakota State Water Commission (SWC) observed increased nitrate concentrations in a quarter of 30 water samples collected from irrigation wells screened in the Englevale aquifer. Four water samples exceeded the EPA Maximum Contaminant Level (EPA-MCL) of 10 mg/L. In response, a meeting was conducted by the North Dakota State Water Commission, with the assistance of the Ransom County Water-Resource District, at the town of Englevale in March of 1997, to define and address the problem. The meeting was attended by area growers, and personnel of the SWC, the Ransom County Water-Resource District, the North Dakota Health Department, and the North Dakota State University Cooperative Extension Service. Cooperative Extension Service personnel discussed and recommended modifying nitrogen management practices, mainly through changing from pre-plant applications to timely applications by fertigation through the irrigation pivots. It was further decided that the SWC would conduct a more extensive investigation of the spatial and temporal trends of nitrate in the aquifer. The purpose of this report is to interpret the results of 11 years of data acquisition by the SWC (1996 through 2006) from the Englevale aquifer. The objectives are to identify the extent of nitrate contamination, and the sources and processes affecting nitrate trends in the aquifer.

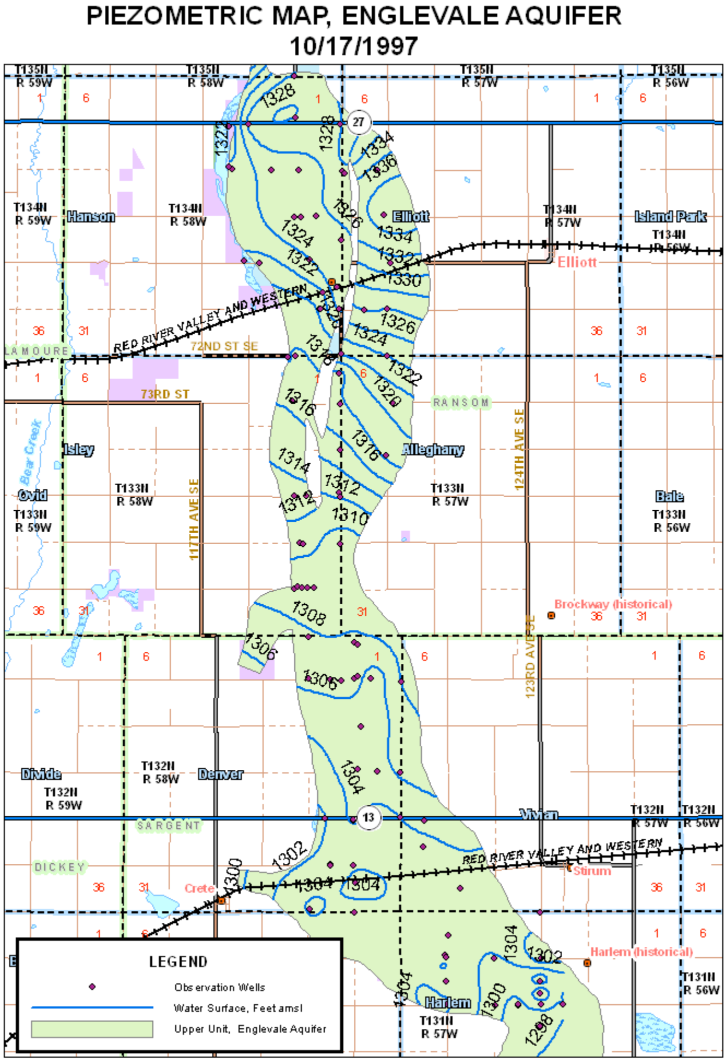
Location and Characteristics of the Englevale AquIfer

The Englevale aquifer is located in western Ransom and Sargent Counties in southeastern North Dakota and extends into northeastern South Dakota (Fig. 1). It was first described by Armstrong (1982) in the Ransom and Sargent County ground-water studies. Preliminary ground-water data, included well logs, water levels, and water quality analysis (Armstrong 1972). The geology of Ransom and Sargent Counties was described by Bluemle (1979). The NDSWC has conducted additional studies of the Englevale aquifer to aid in the management of water resources. Information on SWC test holes, water levels, and water quality are maintained in a web-accessible database at the SWC website (http://swc.state.nd.us/4dlink9/4dcgi/redirect/index.html) under "Map and Data Resources." Logs for privately drilled test holes and water wells are maintained by the Board of Water Well Contractors and are on file at the SWC. They are also available as image files on the cited web-accessible database.

Figure 1. Location of the Englevale aquifer in SE North Dakota.

The hydrogeology of the Englevale aquifer, and its relationship to local climate, was discussed in detail Cline and others (1993). Readers are referred to that report for full treatment. We here summarize briefly some of the major points to help interpret nitrate data presented in this report.

The Englevale aquifer in our study area covers about 44 square miles, 33 of which are in Ransom County, and the remainder in Sargent County. A generic map of the aquifer and flow system for purpose of discussion is shown on Fig. 2. The reader should be cautioned that the aquifer is a dynamic system and that details of the flow dynamics illustrated may be subject to change with changing climate and water use. Rates of ground-water movement are generally less than 600 feet-per-year for coarse gravels, and much less for fine sediments. The northern part of the Englevale aquifer is divided into two channels separated by a till divide (Fig. 2). There is some limited flow across the divide near Englevale. Cross flow may occur as limited water movement through thin surficial sands overlying the till divide, and through dissecting channels.



PIEZOMETRIC MAP, ENGLEVALE AQUIFER
10/17/1997

Figure 2. Piezometric map of upper unit of the Englevale aquifer, interpolated from water-level data collected on October 17, 1997.

The western channel (Fig. 2) is the main channel, and the most productive for irrigation, because of generally larger saturated thicknesses (ranging from about 5 to 120 feet) and large hydraulic conductivities. Hydraulic conductivities from two pump tests were measured at 1,100 ft./d by Reiten (1980) and 600 ft./d by Shaver (1977). Thin saturated zones are most commonly found along the eastern border of the western channel, near the dividing till barrier.

The northern portion of the eastern channel is thinner and finer (fine and medium sand), and serves primarily as a recharge source for the western portions. Cline and others (1993) have recommended that no irrigation withdrawal of water be allowed in the northeastern portion and that it be retained as a recharge source area.

The middle (north-to-south) portion of the Englevale aquifer is narrower in the western channel, with deep (50-to 90-ft.) saturated thicknesses. The eastern channel is thinner ("generally less than 20 feet of saturated thickness"), but some irrigation is developed in narrow local channels. Multiple-well systems are required in this area.

The southern portion of the aquifer consists of a thin surficial unit which is generally too thin and fine to provide adequate pumping rates for irrigation, and a deeper and coarser "very leaky" confined unit (Cline and others 1993). Most irrigation wells in the southern portion of the aquifer are in the deeper confined unit.

Most recharge to the Englevale aquifer is from precipitation. Waters not removed in runoff, and not stored in the soil profile or transpired by plants percolate to the aquifer. Most recharge occurs following spring snow-melts when temperatures are low and evapotranspiration (ET) is low. Least recharge occurs in summer when temperatures and ET are high. Fall recharge exceeds summer due to lower ET. ET removal from the aquifer occurs where the water table is shallow, and also through Lone Tree Lake in the north and the Englevale Slough complex along the western border (and toward the east-west center of the aquifer in the south). Water pumped from the aquifer is usually recovered from decreasing ET caused by lower water tables and decreased proximity to root extraction or surface exposure in wetlands.

Prior to irrigation water levels in the Englevale aquifer were dominated by land surface, and flow occurred mainly within local recharge and discharge cells. In the western portion of the aquifer north of Englevale, flow is mainly southward, toward the Englevale Slough complex. In the eastern portion of the aquifer (east of the till divide) the piezometric gradient is predominantly southward, and discharge occurs through local flow cells of varying path-lengths and with a component of deeper through-flow. In the southern portion of the aquifer, flow is mainly toward discharge zones in the lake and slough complex in the center of the aquifer.

Large-scale irrigation development from the Englevale aquifer began in Ransom County and in Township and Range 132-058 of Sargent County in the mid-1970s. At present about one-third of the Englevale aquifer study area is irrigated. As of 1991 there were 10,800 acres irrigated from the Englevale aquifer in the study areas having a surface area of less than 30,000 acres (Cline and others 1993). This acreage has not increased substantially since 1991. Average water use for 1981 to 1991 from the Englevale aquifer was 9,000 ac.-ft./year. To supply this amount would require that at least 3.6 inches per acre in recharge be captured for irrigation. The average annual application of irrigation water is approximately 10 inches per year, with some deviations for very dry and very wet years, and some variation affected by production practices and commodity prices.

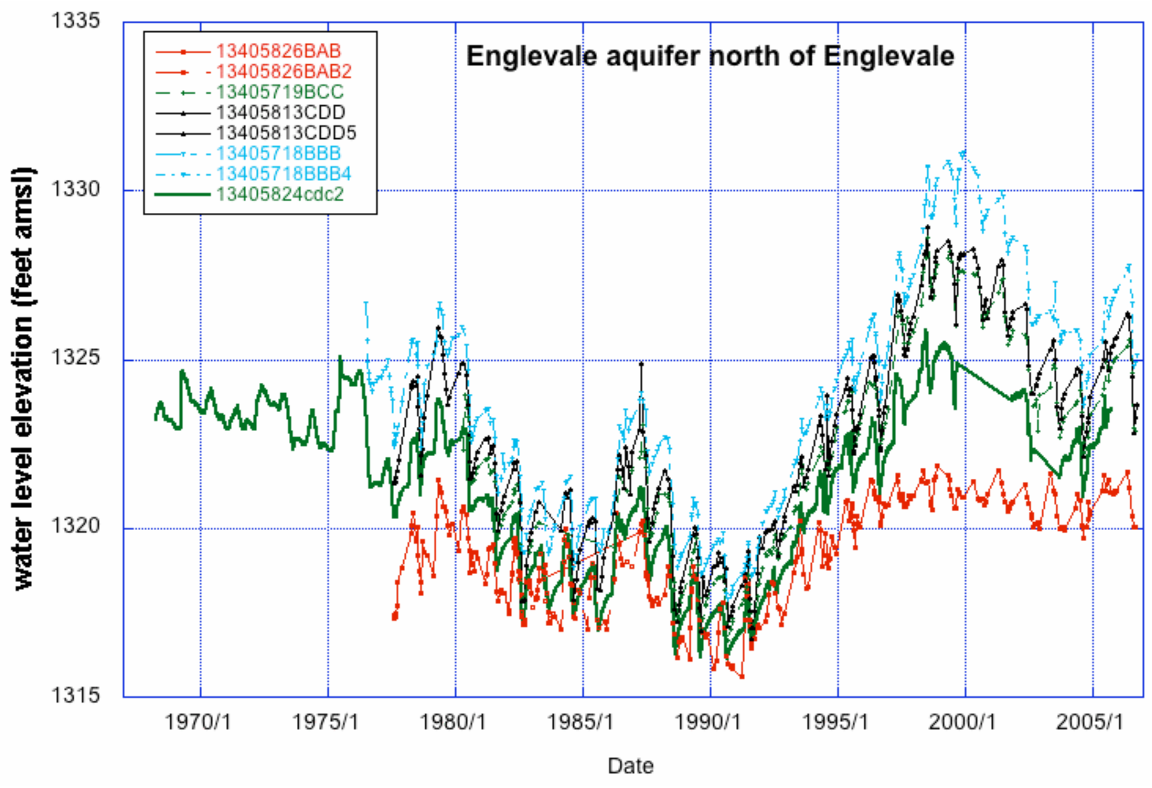


Figure 3. Temporal trends of water-level elevations (amsl) for eight wells at five well sites in the northern (Township 134) part of the Englevale aquifer.

It was concluded from analysis of the 1976 to 1991 period (Cline and others 1993) that the aquifer was over-appropriated with respect to the climate of the 1980s. Using a hydrologic analysis incorporating long-term (1904 to 1989) climate data, however, they concluded that the Englevale aquifer "is not over-appropriated in the long-term, based on Lisbon climatic records from 1904 to 1989." Since that report, the wetter climate in the 1990s affected a full recovery of the aquifer, and a net increase of three to four feet in water levels by 2005 (Fig. 3), compared with pre-development water levels in the 1970s. Water-level trends are illustrated for several well sites on Fig. 3. The figure demonstrates not only the changes in water levels in relation to climate, but the hydrologic dynamics of the aquifer as well. Following 1993 water levels not only increased, but the spread of the head distribution expanded, signifying a more dynamic hydrologic system with renewed movement toward discharge zones. The greatest changes in head occurred in recharge zones, while the least change occurred in discharge zones, such as well-site 134-058-26BAB, located near the Englevale Slough complex, near the western border of the aquifer.

Potential Sources and Processes Affecting Nitrate Concentrations and Loads

Nitrate (NO_3^-) is a highly dynamic anion which has many natural and anthropogenic sources. It is constantly entering and leaving soil and water systems through rainfall, breakdown products of soil carbon cycling, plant removal, microbial assimilation, dissimilation and denitrification, and anthropogenic sources. Most nitrate is cycled within the soil-plant continuum. But when large agricultural inputs are combined with adverse climatic or agronomic conditions, including untimely fertilizer applications, impaired crop uptake or excess precipitation, nitrate can leach to deeper ground water.

Possible input factors likely to affect elevated nitrate concentrations observed in 1996 included: (1) Increased leaching due to recharge events during the early 1990s; (2) expansion of irrigated high-value and intensive agriculture following 1976; (3) common use of untimely (spring pre-plant) fertilizer applications; and (4) climatic conditions non-conducive to optimal crop uptake of nitrate in some years. The main potential offsetting factor affecting input would be nitrate management practices, and more timely nitrogen application, as recommended by the NDSU Cooperative Extension Service personnel.

Possible factors affecting nitrate removal from ground water would include discharge to rivers, springs and wetlands, crop or natural vegetative uptake in areas of shallow water table, or microbial denitrification. Research by Dr. Gale Mayer (1992), and Dr. Scott Korom (2005) and his students at the University of North Dakota (several M.S. and PhD theses), has indicated that many aquifers in eastern North Dakota have substantial amounts of reducing minerals in their sediments, and are capable of removing significant amounts of nitrate through denitrification (reduction to N_2 gas). Both heterotrophic (carbon electron donor) and autotrophic (mineral electron donor) denitrification have been observed in natural ground-water systems.

Previous auger explorations of Englevale aquifer sediments have indicated that they contain substantial amounts of detrital shale, which frequently contain pyrite in eastern North Dakota. It is speculated that denitrification might contribute significantly to the reduction of nitrate in the Englevale aqufer. It is further speculated that interaction of hydrologic conditions with reducing factors might affect nitrate retention and/or removal from the aquifer. For example, the upper strata of an unconfined aquifer is usually highly oxidized because reducing minerals have been removed through long-term exposure to oxygen during water-table fluctuations. Reducing minerals are usually found several feet below the zone of normal water-table fluctuation. It is speculated that under changing climatic conditions, rising water tables would increase the thickness of the oxidized zone and enhance nitrate retention through decreasing proximity to the reducing minerals. Trends of nitrate loading, and effects of climate and the oxidizing and reducing characteristics on aquifer loading and toxicological status are examined in this report.

METHODS

Because most SWC observation wells are screened near the bottom of the aquifer, the Englevale aquifer monitoring-well network was enhanced by 91 wells, nested in 29 sites during 1996 and 1997 to further identify and monitor the spatial distribution of nitrate, and to identify the temporal trends of nitrate concentrations, and the physical, chemical and hydrologic factors affecting those trends. The network was designed and constructed by Royce Cline of the SWC. The objectives of the expanded monitoring-well network were: (1) For each site, wells screened at the water table, at 10 feet below the water table, and at 20 feet below the water table; and (2) a five-foot screen across the water table for the shallow well, to allow for water-table fluctuation. In addition, a fourth well was added to enable water-table sampling at some sites where large rises in the water table occurred. Deeper wells were installed at some sites unrelated to the nitrate study (ex. 132-058-13CCC and -35AAA). The number of wells per site ranged from one to seven, although the maximum and minimum were single well sites, and most nests contained two or three wells. The median and mean of wells constructed per site were both three. Well screened intervals were mostly 2.5 or 5 feet, with some local variation. Thirty well sites were selected for use in analysis of nitrate-N loading and dissipation trends, and for assessment of toxicological trends.

Data Collection and Measurement

Wells were sampled, under the supervision of Royce Cline of the SWC, in November-December 1996, June, August, September and November of 1997, June, July, September and November of 1998, October of 1999, September of 2000, and in October to early November of 2001 through 2006. Water samples were collected using a screw pump, or a bailer, depending on well characteristics. A minimum of three well volumes were evacuated before sampling. Electrical conductivity (EC), water temperature and pH were measured on-site. All dissolved oxygen (DO) measurements were collected using a YSI Model 85 downhole DO meter. Bicarbonate (HCO_3^-) and electrical conductivity (EC) were determined using the raw untreated 500-ml sample. Sulfate (SO_4^{2-}), flouride (F^-), chloride (Cl^-), and dissolved solids (DS) were determined using the filtered (0.45 μ) water sample. Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) were determined using the filtered (0.45 μ) and acidified (2 ml-nitric acid) sample. A Perkin-Elmer Model 4000 atomic-adsorption spectrophotometer was used to measured concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Mn^{2+}, Li^+, and Sr^{2+}. Orion Model 960 and 940 titralyzers were used to measure concentrations of HCO_3^-, CO_3^{2-} and Cl^-. A gravimetric method was used to measure the concentration of SO_4^{2-}. Flouride (F^-) was measured using a specific iron electrode. Water samples for nitrate were preserved with 2 ml-sulfuric acid.

Data Processing and Interpretation

There are four main problems involved with interpreting the significance of large vertically stratified sets of data in a setting like that obtained for Englevale. These are:

(1) Vertically stratified data are complex and very difficult to apply for straightforward surficial spatial interpretation and comparison. Integration and simplification is therefore needed to provide an intelligible basis for analysis. Most North Dakota ground water is vertically stratified with respect to nitrate, having periodic large concentrations near the surface (Mayer 1992, Patch and Padmanabhan 1994, Olson, 1992, Bartelson and others 1993-2005[1], Schuh and others 1997, Schuh Bottrell and Korom 2006, Casey and others 2002, and others), and decreasing - frequently logarithimically (Schuh and others 1997) with depth. Usually the nitrate is fully dissipated within 10 to 20 feet of the aquifer surface, sometimes less. This depends on many processes, including denitrification. This process and its contribution to the Englevale aquifer nitrate status will be discussed in detail later in this report.

(2) In a stratified setting, applying a toxicological standard based on human health and consumption such as the EPA-MCL of 10 mg/L nitrate-N (44 mg/L nitrate as nitrate) is difficult. If the object of a standard is human consumption, then the significance of the standard with respect to well intake must be considered. For example, an aquifer having a large concentration of nitrate in the top five feet, would have little toxicological significance for an aquifer having a saturated thickness of 80 feet and a well screened in the bottom half of the well unit. Some adaptation is necessary to account for the relationship between the vertical distribution and actual beneficial use of the water.

(3) The quantitative relationship of contamination to agricultural sources must be considered. Normal concentration units for ground water are noninformative with respect to agricultural applications. A means for cross interpreting toxicological and agricultural standards is needed in order to translate contaminant status to units that can be related to fertilizer management and the on-field economic ramifications of nitrate loss.

(4) The spatial interpretation of local measurements is a formidable problem. Using point data from wells to interpret environmental outcomes of agricultural practices

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[1] North Dakota Groundwater Monitoring Program Annual Reports (1993-2005), North Dakota Department of Health, (Unavailable for public viewing because of state privacy laws).

requires an understanding of the relationship between local measurements and surrounding areas. If they are spatially dependent then mapping procedures can be used to integrate measurements. If not, then random statistical representation is most appropriate.

Interpretive Metrics

To accommodate these needs two metrics are used. They are: (1) nitrate-N load; and (2) an index of toxicological significance which we call the "Potential Mixed Concentration Index" (PMCI).

(1) Agricultural Application Standard: Nitrate-N Load

The purpose of the nitrate-N load parameter is to provide a single integrated index for each measurement site that can provide a consistent metric for temporal change, a metric for cross comparison of sites, and can be compared to units of agricultural application. Steps in computation are as follows:

Nitrate-N concentration (N) is computed from measured nitrate concentration ($NO3^-$) using mass conversion:

$$N\left(\frac{mg}{L}\right) = 0.226 \bullet NO_3^-\left(\frac{mg}{L}\right) \qquad (1)$$

Total nitrate loading(N_t^*) is first computed by integrating nitrate concentrations (mg/L) over depth (feet) as:

$$N_t^* = \int_o^z N dz \qquad (2)$$

which results in units of mg-ft./L. This cross-standard, and somewhat uninformative unit is converted to pounds total-N per-acre (N_t) by employing a series of appropriate conversion units, and adjusting for porosity, since the grain matrix does not contain nitrate. An estimated total porosity of 0.4, which is common for sands, is used. The conversion is:

$$N_t\left(\frac{lb.}{a}\right) = N_t^*\left(\frac{mg-ft.}{L}\right) \bullet 10^{-6}\left(\frac{kg}{mg}\right) \bullet 10^{3}\left(\frac{L}{m^3}\right) \bullet 4.047 \bullet 10^{3}\left(\frac{m^2}{a}\right)$$
$$\bullet 0.3048\left(\frac{m}{ft.}\right) \bullet 2.21\left(\frac{lb.}{kg}\right) \bullet 0.4\left(\frac{m^3}{m^3}\right) \qquad (3)$$

The final units can be checked by cancellation using dimensional analysis. Equation 3 simplifies to:

$$N_t\left(\frac{lb.}{a}\right) = 1.09\frac{lb.-L}{a-mg-ft.} \bullet N_t^*\left(\frac{mg-ft.}{L}\right) \qquad (4)$$

or a simple conversion factor of 1.09. This can be modified for varying porosity (η) assumptions by multiplying by $\frac{\eta}{0.4}$.

In addition to providing a useful, consistent, and comparable management index, the nitrate-N load density is robust with respect to well nest depth configurations, since computations do not depend on the specific depth distribution of wells. Examples are provided in Fig. 4 from previous work on the Karlsruhe aquifer. Fig. 4A (left) shows a plot of N_t versus depth. Regardless of specific measurement intervals or depths below the water table, cumulative values usually eventually level off at some depth below the water table. This occurs at the maximum depth of significant nitrate penetration. This maximum value is the estimator of N_t.

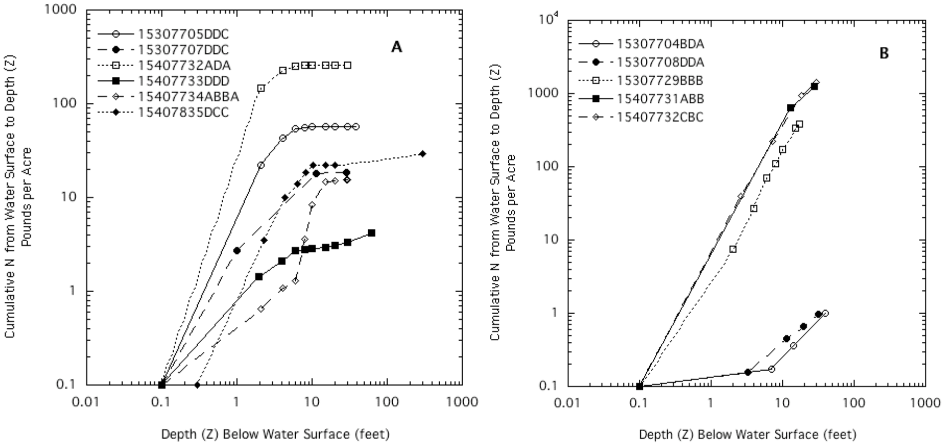

Figure 4. Cumulative nitrate load density with depth, in lb./ac. for: (A) selected multi-port samplers and (B) selected well nests.

Figure 4B (right) shows some data that have not yet reached constant values at the maximum measured depth. This can occur for two reasons. The first possibility is that the substantial nitrate has penetrated to the bottom of the aquifer so that no plateau can occur in the integral values. In this case, the N_t measurement is a "true" measurement, in that it provides an estimate of actual total loading. The second possibility is that nitrate has penetrated beneath the level of the maximum sample point. In this case, the maximum calculated value must be considered as a "minimum" nitrate load. Since most of the aquifer has been measured in each case, and the (upper) portion measured is almost invariably most contaminated, the additional N unaccounted for is likely small. For example, on Fig. 1B measurements at sites T 154 N, R 77 W, Section 31ABB and T 154 N, R 77 W, Section 32CBC are both indeterminate, but both show indications of approaching maxima. Sites with these characteristics are used with the understanding that they impart a slightly conservative (low load) bias to final estimates. In any case, judicious familiarity with the site and its characteristics is essential for proper use and interpretation of the index.

All integrations were performed using the mid-point method. Because of variations in site design and variance in the water table, practical decisions must be made in applying the data. For each well the measured concentration is applied to both the top and bottom of the well screen. If the water table is below the top of the shallowest well screen, then the ambient water-table is the top measurement point. If the top of the well screen is more than 5 feet beneath the water table for a given sample date, the data for that data is not included. If, examining the data, a deeper well has negligible or non-detectible nitrate, and there is a large interval between the well and an overlying well with significant nitrate concentrations, the deeper well data is discarded, because without demonstrable vertical dependence with overlying wells, interpolation could cause serious overestimation. Single wells are used if the aquifer is thin, subject to above-explained restrictions. In cases where well screens spanned the aquifer, or where the bottom of the well screen was on the bottom of the aquifer and spanned most of the aquifer to within five feet of the surface, integration (Eq. 2) was performed using a simple multiple of saturated thickness.

The precision of calculations depends on the density of vertical sample representation and should be considered general in nature and suitable for broad comparisons. Generally the data should be interpreted as minimum loads. For example, a site with shallowest well screen at 4 feet below land surface will be used, but will often fail to represent the contribution of the maximum nitrate concentration, which is usually within the top three to four feet. Spatial bias, in most cases, is toward underestimation rather than overestimation. Temporal comparisons within the site should be considered more robust than spatial interpretations.

The output, in lb./ac. or kilograms per hectare, can be compared to agricultural applications. An approximate economic value can be assigned, based on fertilizer cost. Costs vary from about $0.35-$0.40 (June 2008) per unit N for anhydrous ammonia (80-0-0), to somewhat higher costs for urea (46-0-0), diamonium phosphate (DAP, or 28-46-0) and urea-ammonium nitrate (UAN, or 28-0-0) sources. These vary considerably between times, locations, and individual operations and their volume discounts.

(2) Toxicological Standards: Potential Mixed Concentration Index (PMCI)

Toxicological concerns and resulting regulatory limits are usually framed within concentration boundaries set by the U.S. Environmental Agency (EPA) called Maximum Contaminant Levels (MCL). Some states choose to adopt their own, more stringent, standards for some contaminants. The state of North Dakota under NDCC Sec. 33-17-01-06 has accepted EPA standards. The MCL for nitrate is 44 mg/L expressed as nitrate (mol. wt. 62 g/mole,) or 10 mg/L expressed as N equivalents (14 g/mole). The basis for toxic concern is a condition called methemoglobinemia, caused by nitrate reduction in the intestinal tract to nitrite which then impairs the blood's ability to transport oxygen (Fetter 1980). The condition occurs most commonly in fetuses or in infants less than three months of age, hence the alternate name, "blue baby syndrome." It is potentially fatal if not remedied.

Reasonable implementation of concentration-based ground-water regulations is complicated by common stratification of nitrate in aquifers (Mayer 1992). Nitrate-N commonly occurs at relatively high concentrations (even above MCL) in surficial portions of aquifers under a wide range of natural and anthropogenic conditions and practices. However, this may or may not pose a serious problem for the aquifer as a water supply. Toxicological concerns are governed by the nitrate loading rate (how fast nitrate is being added and in what amounts), the aquifer nitrate dissipation rate (discharge or denitrification), and factors, usually pumping practices, affecting the mixing of the aquifer. Some aquifers are capable of removing substantial nitrates through autotrophic denitrification, and are characterized by large nitrates in a very limited portion of the upper aquifer that is oxidized (Mayer 1992). Some aquifers discharge toward unoxidized wetlands that are rich in organic matter and capable of heterotrophic denitrification. Others, like portions of the Oakes aquifer near Oakes, ND, are capable of discharging stratified nitrate-laden waters through tile drains (Olson 1992). If removal rates are capable of offsetting loading rates, or if high nitrate concentrations are shallow and local, and are of insufficient quantity to result in substantial degradation of the aquifer as a whole, then stratified nitrate is not likely to be a serious threat to health or environment. Conversely, if loading rates are much larger than removal rates, and if quantities entering the upper strata are sufficient to cause the aquifer itself to be threatened once mixed by pumping, regulatory concern becomes more compelling.

One informative index for evaluating the toxicological significance of nitrate loading at any location is the relationship or ratio between total N and the volume of water in the aquifer. An index called the "Potential Mixed Concentration Index" (labeled PMCI) is calculated as total local nitrate-N load (N_t^* in Eq. 2), divided by the local saturated thickness of the aquifer (Eq. 5). This index represents the potential nitrate-N concentration of the entire thickness of the aquifer if it were to be thoroughly mixed, as would be approximated with a fully penetrating high-capacity irrigation well.

$$PMCI\left(\frac{mg}{L}\right) = \frac{N_t^*\left(\frac{mg - ft.}{L}\right)}{h} \tag{5}$$

for saturated thickness h.

The PMCI does not predict the concentration of any specific local well. A shallow well might yield water of much higher concentration, while a well with deep screened interval might yield water of much lower concentration. Rather, it indicates the mean toxicological potential for a given location under conditions conducive to mixing, such as in a fully penetrating irrigation well. It answers the question: **"is there enough nitrate in the aquifer to cause the entire aquifer at this location to exceed the EPA-MCL under worst-case conditions?"**

The aquifer saturated thickness used for calculating the PMCI was estimated using local water-level measurements corresponding to the time of nitrate-N sampling, and the local depth to the aquitard recorded on the drill logs for the site.

RESULTS

Thirty of the well sites and irrigation wells were selected for evaluation using the nitrate-N load and PMCI parameters (Fig. 5). Analyses include: (1) an overview of nitrate contamination status and identification of sites of greatest concern; (2) an examination of climatic effects on temporal changes in nitrate load; (3) an assessment of the role of denitrification in dissipation of nitrate; (4) a site-by site analysis of loads, loading trends, PMCI, and loading and dissipation factors affecting individual sites; and (5) an estimate of the spatial distribution of nitrate-N load based on interpolated maps for irrigation and observation wells. A summary of soil classifications, well-site hydrologic characteristics, shallow nitrate concentrations, and nitrate-N load and PMCI is provided on Table 1.

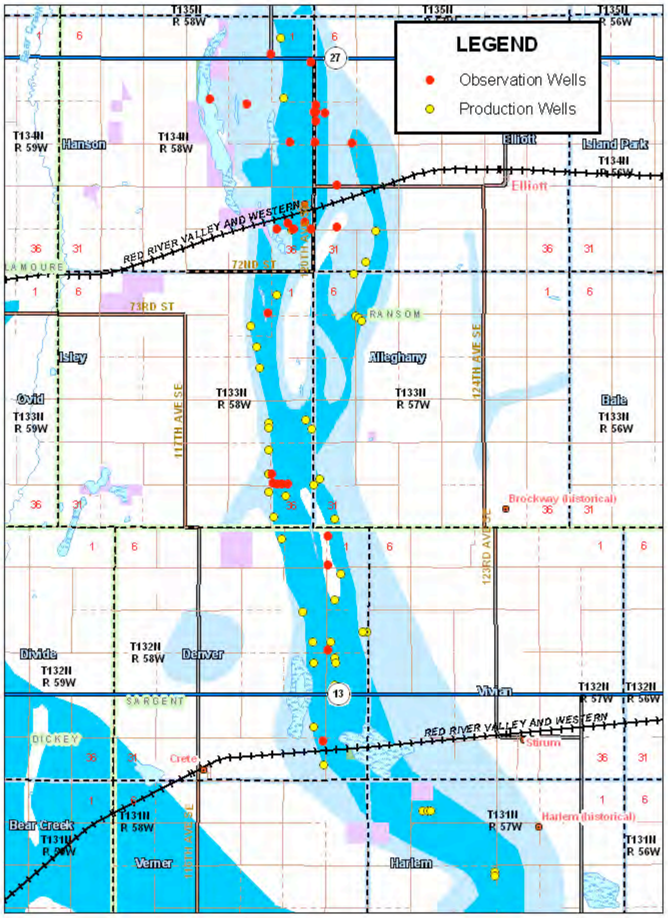

Figure 5. Locations of well nests (red) and Irrigation Wells used for nitrate evaluation.

Table 1. Summary of well-site shallow nitrate concentrations (as nitrate), nitrate-N loads (as N), PMCI, with site soil and hydrologic characteristics.

Location	WT depth (range) feet	WT depth (median) feet	Aquitard depth feet	Sat. Thick (range) feet	N-Load (Range) lb./acre	N-load (median) lb./acre	PMCI (Range) mg/L	PMCI (median) mg/L	Shallow Nitrate (range) mg/L	Soil Mapping Unit
13205801BBC	1.81-7.6	4.78	30	22.4-28.19	0.6-88	14.7	0.02-3.3	0.53	0.2-60.2	Glyndon
13205801CCC	10.9-16.08	13.59	31	14.92-20.1	37-269	59	1.7-13.4	3.3	17-127	Spottswood
13205813CCC	8.8-13.1	11.03	63	49.9-54.12	5-335	93	0.09-5.7	1.6	10.3-220	Spottswood
13205835AAA	15.14-19.6	17.73	58	38.4-42.86	167-459	251	4-10.8	5.6	0.2-140	Gardena/Glyndon
13305825CBCC	14.1-18.6	16.74	50	24.37-34.6	0.6-431	25	0.0-15.8	0.84	0.1-180	Sioux/Renshaw
13305825CCC	17.5-22.7	20.72	61	4.17-40.28	179-355	259	4.2-7.9	5.72	36.6-180	Sioux/Renshaw
13305825CCDC	8.9-13.83	11.86	43	29.22-30.09	27-172	89	0.8-4.8	2.6	26-172	Sioux/Renshaw
13305825CDCC	3.19-8.05	5.88	57	48.95-53.81	6-36	24	0.04-0.64	0.38	2.92-20	Divide
13305825CDDC	0.76-5.61	3.18	36	30.39-35.24	0.6-2.2	0.7	0.017-0.063	0.019	0-1	Divide/Arveson
13305802DDD	14.62-18.7	16.35	36	17.3-21.38	17-316	152	0.86-15.1	7	11-170	Sioux/Renshaw
13405718BAC	11.39-17.47	15.47	28	10.53-16.61	13-182	103	0.87-13.5	7	0-48	Renshaw/Sioux
13405718BBB	13.22-19.87	16.76	41	21.13-27.78	25-255	62	1-10	2.2	2.7-100	Renshaw/Sioux
13405718BBCC	13.25-19.23	15.45	46	26.77-32.75	67-1241	376	2-34.8	10.6	12-160	Sioux/Renshaw
13405718BBCCD	15.47-22.16	18.18	44	21.84-28.53	0.6-826	470	0.02-28.7	16.5	25.3-150	Sioux/Renshaw
13405718BCC	13.1-20.6	16.18	46	25.84-32.9	20-503	162	0.7-15.3	6.8	7-87	Renshaw/Sioux
13405718CCC	12.21-19.04	15.26	42	22.96-29.79	141-576	382	4.8-21	14.6	6-110	Renshaw/Sioux
13405718DDD	3.3-8.2	5.73	32	23.8-28.72	19-351	246	0.7-12.3	8.37	11.9-170	Renshaw/Sioux
13405719DCC	2.75-7.97	4.58	20	12.03-17.25	4-48	11	0.28-3.7	0.67	0.18-25	Sioux/Renshaw
13405730DCC	3.8-11.43	9.31	20	8.57-16.2	12-261	48	3.7-82	16.7	3.7-35	Sioux/Renshaw
13405825CCD	9.2-11.55	10.51	83	71.45-73.8	29-116	78.99	7.8-31.5	21.3	81-220	Brantford/Coe
13405825CDAC	8.04-10.2	8.81	76	65.8-67.96	72-300	186	1.2-4	2.4	7.9-164	Renshaw/Sioux
13405825DCCC	17.57-20.4	19.09	57	36.6-39.43	618-1852	1069	17.7-43.5	25.7	130-230	Brantford/Coe
13405825DCCCD	15.92-19.06	17.55	26	6.94-10.08	70-184	88	7.1-18.4	9.7	67-122	Brantford/Coe
13405825DDB	9.82-12.81	11.09	23	10.19-13.18	229-677	318	19.6-48.8	25.9	30-320	Brantford-Vang
13405825DDDDC	7.44-11.8	9.2	21	9.2-13.56	8-33	18	0.5-3.3	1.3	12904	Renshaw/Sioux
13405801CCB	19.29-25.94	21.82	30	1.06-10.71	6-107	41	1.3-14	4.9	8.4-86.8	Sioux/Renshaw
13405810DCC	12.53-14.0	13.41	24	10-11.47	9-97	59	0.79-8.5	4.73	4.3-57	Southam scl
13405812AAA	17.03-24.36	20.7	74	49.64-56.97	45-249	1.7	4.3-57	12	0.02-17.8	Renshaw/Sioux
13405813CDD	16.15-22.1	18.9	141	118.9-124.85	7-297	59	0.05-2.2	0.44	3.5-149	Renshaw/Sioux
13405814BAA	9.7-13.3	11.5	24	10.68-14.3	0.15-14	0.23	0.01-1	0.02	0-2.25	Sioux/Renshaw

Overview of Nitrate Contamination Status in Observation Wells

To reasonably interpret and compare nitrate contamination on individual well sites, it is useful to establish a basis for designating what is a "low" or "high" load. For the purpose of our discussion we will use the PMCI as the primary reference. Anything above the EPA-MCL of 10 mg/L will be designated as "high." In a survey of mid-western wells Burkhardt and Kolpin (1993) estimated a maximum nitrate-N concentration of 3 mg/L for wells unaffected by anthropogenic influence, so we will designate all PMCI below 3 mg/L as very low. Considering that the PMCI is based on a theoretical uniform contamination of the entire thickness of the aquifer, and lies at the limit of a toxicologically based standard, we suggest that a desirable goal should be less than the limit. Somewhat arbitrarily for the purpose of this report we will place that goal at half the EPA-MCL (5 mg/L). Thus, we will label as "low" all PMCI such that 3 mg/L < PMCI < 5 mg/L; and as "moderately high" all PMCI such that 5 mg/L < PMCI < 10 mg/L.

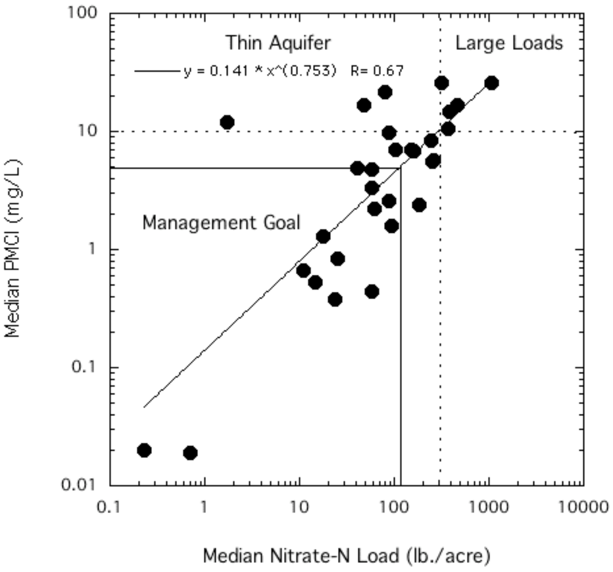

Figure 6. Relationship between the toxicological standards and loading rates.

The PMCI is affected by both nitrate loading and aquifer thickness. Thus, depending on the cause, it may be an indicator of either aquifer vulnerability (susceptible to high concentrations at small loads because of its thinness), or of large nitrate influx, sufficient to influence even thick aquifers. We can examine these relationships by plotting median PMCI and median nitrate-N loads (Fig. 6). For PMCI vs. nitrate-N load, a power function best approximates a normal and equivariant distribution. Applying the power function for the Englevale data, moderately high equivalent nitrate-N loads based on PMCI standards are: 120 lb./ac.<nitrate-N load<310 lb./ac., and the transition to high loads occurs at about 310 lb./ac. Using this same relationship, vulnerable aquifer sites can be indicated as the union of: PMCI> 10 mg/L and nitrate-N load < 310 lb./ac.; and high load sites can be indicated as the union of: PMCI > 10 mg/L and nitrate-N load > 310 lb./ac. This relationship is specific to the Englevale aquifer, and might differ considerably for another aquifer having a different distribution of saturated thicknesses.

Without consideration of temporal trends, and based on median values for all thirty well sites from 1996 (1997 for some sites) and 2006 (2005 for some sites), three well sites (10%) would be considered unsuitably high in nitrate because of vulnerability, four (13%) would be considered unsuitably high because of excessive loading, eight (27%) would be considered moderately high, and 15 (half) would be considered low to very low in nitrate. An additional benefit of this interpretive scheme is that it incorporates a loading range that corresponds well with commonly used agricultural applications. Fertilizer applications between 100 and 300 lb./ac. encompass fairly well the normal application range for crops under high-value production agriculture. The economic ramifications of high PMCI from a toxicological standpoint correspond very well with the loss of a one-to two-year application of fertilizer on the crop. These are summarized on Table 2.

Table 2. Response matrix used for interpretation of the contaminant status of Englevale aquifer well sites. VL is very low, L is low, MH is moderately high, H is high, VV is very vulnerable, V is vulnerable, and SV is somewhat vulnerable.

Nitrate-N load (lb./ac.) / PMCI (mg/L)	0-50	50-120	120-310	>310
0-3	VL	VL	VL	VL
3-5	L	L	L	L
5-10	MH	MH	MH	MH
>10	H/VV	H/V	H/SV	High load

It is also useful to examine the overall temporal trends (improving or deteriorating) of aquifer nitrate. A comparison of initial (1996-1997) and final (2005-

2006) nitrate-N loads and PMCI indicated that about 65% of all sites improved over the measurement period, and the median improvement was 40%. A matrix comparing final objective contaminant status (final PMCI) and improvement status is illustrated on Fig. 7. Results from Fig. 7 are presented on Table 3. They indicate that seven sites have ending PMCI over the EPA-MCL of 10 mg/L, but are improving (median improvement about 39%). Three sites are above EPA-MCL and are deteriorating. And three sites are between 5 and 10 mg/L and are deteriorating. Areas near all of the sites on the table should be carefully monitored. Those designated as >10 mg/L/D (above EPA-MCL and deteriorating) should be treated with particular care.

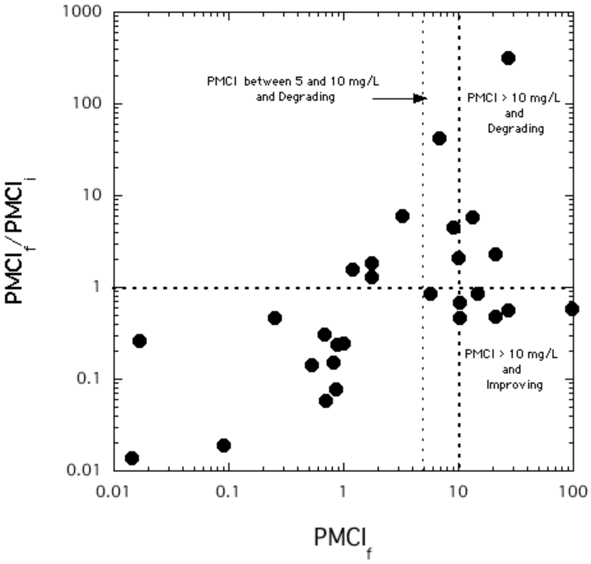

Figure 7. Toxicological classification of Englevale well sites based on PMCI.

Relationship Between Nitrate-N Load Trends and Climate Trends

A plot of mean and median nitrate-N loads (Fig. 8), for all available data with annual winter (October through April) and summer (May through September) precipitation (P) data, indicates a close similarity between data traces for nitrate-N load and precipitation, with increasing P corresponding to increasing nitrate-N load. Similarities are strongest between median and mean values and winter precipitation. Climatic data indicated a gradual increase in summer P throughout the 1980s, but the most distinctive component of the "wet" 90s, from 1993 through 1997, was the increase in winter (and spring) precipitation. The apparent nitrate-N load vs. P correspondence before 1996 is unreliable because most of the Englevale observation wells were screened in the lower aquifer. There was only one well nest with a well sufficiently near the surface to represent each of 1976, 1987 through 1990, 1992 and 1993. However, correspondence between elevated nitrate-N load measured in 1996 on the single load measurement site and elevated summer P, while sparse, supports the relationship established using later and larger data sets. In 1996 and 1997, 29 additional well nests were constructed or augmented. This was the first year of large measured nitrate-N load values.

Table 3. Nitrate contaminant status for well sites of concern. "I" indicates improving, "D" indicates deteriorating.

Location	Initial Load (lb./ac.)	Initial PMCI (mg/L)	Final Load (lb./ac.)	Final PMCI (mg/L)	Nitrate-N load_f / Nitrate-N load_i	PMCI_f / PMCI_i	Nitrate Contaminant Status
13405825CCD	82.11	22.1	37.6	10.3	0.458	0.465	> 10 mg/L / I
13405825DCCCC1	1852	43.5	843	21.1	0.455	0.485	> 10 mg/L / I
13405825DCCCD1	18.42	165	11.6	96.9	0.630	0.587	> 10 mg/L / I
13405825DDB1	677.1	48.8	349	27.3	0.515	0.559	> 10 mg/L / I
13405718BCC3	503.1	15.3	299	10.4	0.595	0.679	> 10 mg/L / I
13405718CCC4	518.2	17.7	382	14.9	0.737	0.841	> 10 mg/L / I
13405801CCB	10.79	9.38	32.3	21.2	3.00	2.26	> 10 mg/L / D
13405718BBCCD1	2.402	0.0853	692	27.0	288	316	> 10 mg/L / D
13205801CCC3	42.16	2.28	269	13.3	6.38	5.87	> 10 mg/L / D
13405718BBCCC1	67.04	2.04	300	9.14	4.48	4.47	5-10 mg/L / D
13305825CBCC2	5.747	0.161	233	6.80	40.5	42.3	5-10 mg/L / D
13205835AAA7	207	4.73	417	9.97	2.01	2.1	5-10 mg/L / D

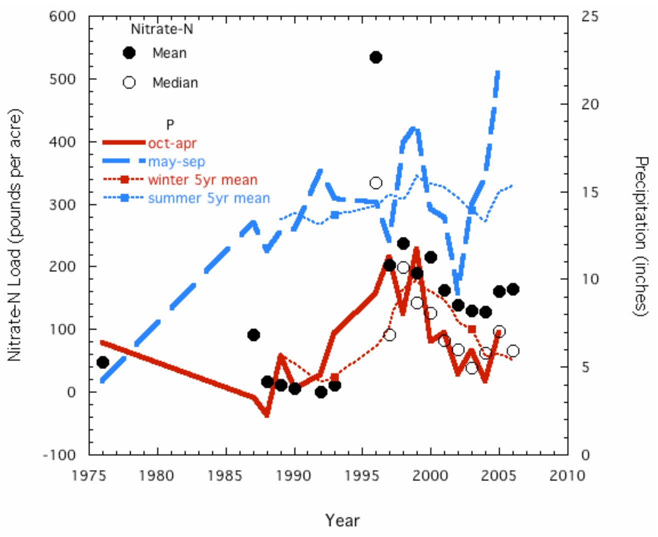

Figure 8. Measured mean and median nitrate-N loads and seasonal precipitation summaries for 1975 through 2006.

A climatic precondition which may have increased nitrate loss was the cool, wet summer of 1992. According to State Climatologist, John Enz (Oct. 29, 1992), most of the eastern third of North Dakota was more than five degrees below normal during the 1992 summer growing season, resulting in 600 fewer than normal Growing-Degree Days. Delays in crop growth, as exemplified by delayed wheat and harvests, likely limited fertilizer uptake. This, in turn, would have exposed spring-applied nitrogen to leaching from 1992 summer rains in areas of coarse soils, and particularly irrigated coarse soils like those near Englevale. Where crop uptake was impaired, it would also have caused the retention of residual nitrate, which would have been available for leaching during the wet summer of 1993. According to Enz (August 13, 1993) precipitation from May through July rainfall averaged more than 200% of normal for the entire state, and exceeded 300% in some areas. Large rains in 1993, combined with below average temperatures, following slow crop growth in 1992, likely initiated the nitrate flush. Leaching was likely then enhanced by normal rainfall in 1994 and above normal July rainfall in 1995 (Enz and Brenk, Oct. 20, 1995).

From 1998 through 2006 a decreasing nitrate trend, corresponding to decreasing P is discernible. For consistency of sample set we will confine our analysis of nitrate-N load trends to the period of 1997 through 2006. The number of samples representing each year vary from 21 to 39, due to multiple measurements at some sites in some years. Plots of mean, median, maximum and minimum nitrate-N load (Fig. 9) indicate a predominant downward trend in N load, with a slight recovery in 2004-2006. These correspond with precipitation data, and an apparent best correspondence with winter P.

Significant ($p<0.05$) decreasing trends for mean and median N load are exponential, indicating that the rate of dissipation is likely concentration dependent. Mean nitrate-N load in 2006 was 64% of that in 1997, indicating a total dissipation of 36%, or an average of about 4% per year. Median nitrate-N load dissipation was more substantial, at 42% of the 1997 nitrate-N load in 2005. This indicated a total dissipation of 68% of the median 1997 nitrate-N load, or about 8% per year. The rate of maximum measured nitrate-N load decrease is similar to the mean. Trends in minimum values are statistically non-significant, and are all less than one pound per acre. Given variability of field measurement these would not be statistically different from zero and will be considered as equivalent to zero loading.

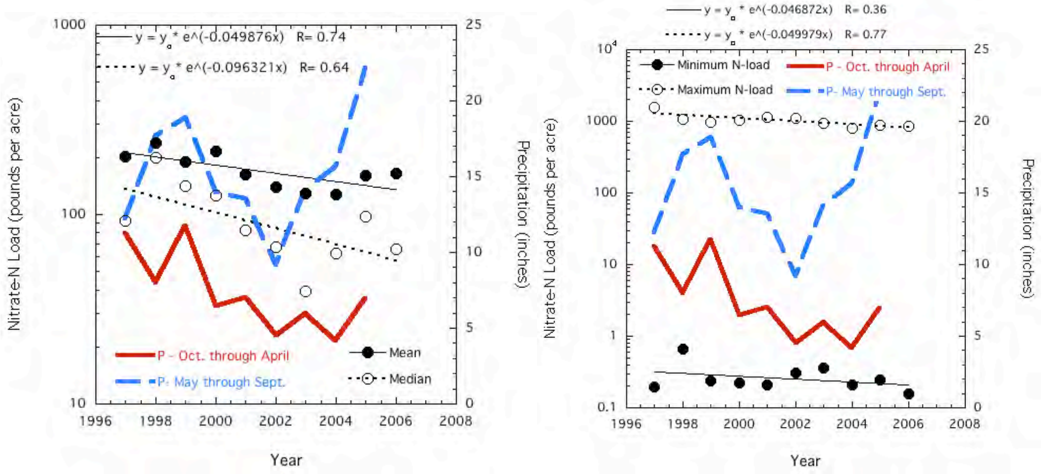

Figure 9. Comparison of trends in mean and median (left) and maximum and minimum (right) nitrate-N loads with seasonal precipitation.

Because the observed trends are exponential, nitrate-N load is decreasing at a decreasing rate. The percent-per-year dissipation is thus decreasing with time and likely with concentrations. Such processes, described as "first-order decay" processes, are common with biologically-based dissipation models. Nitrate-N load dissipation rates can be compared with those of the Karlsruhe aquifer, which has been extensively investigated from 2001 through 2006 using between 60 and 70 well nests. Karlsruhe well trends, shown on Figure 10, are very similar to Englevale trends for the same period. Initial total estimated load for the Karlsruhe aquifer was about 4 million pounds, and it declined to about 3 million pounds by 2006. The exponential dissipation function indicates that about 29% of the nitrate was dissipated between 2001 and 2006, with an approximate dissipation rate of about 6% per year. This is within the range of median and mean values measured for the Englevale aquifer.

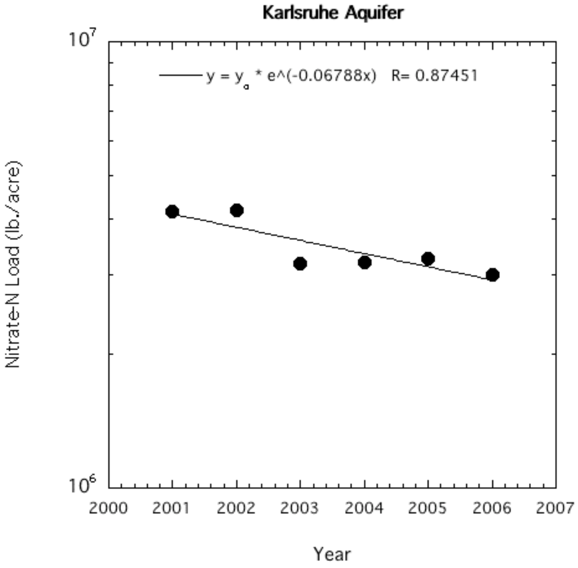

Figure 10. Nitrate-N load dissipation in the Karlsruhe aquifer from 2000 through 2006.

Climatic Effect on Nitrate-N load

For evaluation of climatic effect, it is useful to examine the direct relationship between nitrate-N load and climatic variables. Correlations for nitrate-N load with P and a temperature-based estimation of the Penman-Monteith model for potential evapotranspiration (PET), as standardized by the ASCE (ASCE, 2001), are shown on Table 4. The nitrate-N load vs. P and ET relationships are predominantly linear. Climatic data used are for 1997 through 2005. Thresholds of significance for correlation coefficients with six degrees of freedom are $r = 0.707$ for $p<0.05$ (Snedecor and Cochran, Table A 11, p 557) and about 0.61 for $p< 0.1$.

Both end-weighted and centered five-year moving average P were correlated with nitrate-N load. Centered moving averages provided the highest correlation ($r=0.86$ for the centered average vs. 0.63 for the end-weighted average. The strongest significant correlation ($p<0.05$) of precipitation with nitrate-N load is the five-year moving average winter and spring P. About 74% of the mean nitrate-N load can be predicted by the winter-spring mean P value alone. The second strongest correlation is with the five-year total P value. Correlations with growing-season P are positive, and in some cases substantial (Maximum nitrate-N load vs. single-year summer P values). But they are all non-significant at $p < 0.05$. These would indicate, physically, that the flushing of nitrate-N is likely occurring in the spring recharge event following snowmelt and frost dissipation. This concurs with the timing of the main recharge events described by Cline and others (1993). It is also the time when the water table is shallowest.

Table 4. Pearson Product-Moment Correlation for nitrate-N load vs. annual October through April precipitation (P-W), five-year average annual annual October through April precipitation (P-W-5), annual May through September precipitation (P-S), five-year average annual May through September (P-S-5), total annual precipitation (P-T), five-year average total annual precipitation (P-T-5), annual October through April potential evapotranspiration (PET-W), five-year average annual October through April potential evapotranspiration (PET-W-5), annual May through September potential evapotranspiration (PET-S), five-year average annual May through September potential evapotranspiration (PET-S-5), total annual potential evapotranspiration (PET-T), and five-year average total annual potential evapotranspiration (PET-T-5). Yellow = significant difference at $p<0.05$, green = significant difference at $p<0.1$.

	Mean	Median	Max	Min
P-W	0.597	0.485	0.549	-0.045
P-W-5	0.857	0.707	0.660	0.248
P-S	0.196	0.430	-0.508	0.164
P-S-5	0.189	0.214	-0.101	0.008
P-T	0.446	0.563	-0.097	0.098
P-T-5	0.772	0.666	0.469	0.199
PET-W	-0.358	-0.269	-0.666	-0.242
PET-W-5	-0.776	-0.557	-0.776	-0.197
PET-S	-0.045	-0.089	0.172	0.392
PET-S-5	-0.606	-0.556	-0.514	-0.311
PET-T	-0.315	-0.277	-0.404	0.093
PET-T-5	-0.796	-0.612	-0.764	-0.254

Strong negative correlations of nitrate-N load with PET (Table 4) would likely be related to surrogate correlations of PET with P as indicators of cloud cover and lower temperatures caused by evaporation (latent heat) during periods of high moisture, and indicators of P availability for recharge, through lack of evaporation and sublimation. Strong negative cross correlations of P and ET are shown on Table 5.

The linearity and strength of the nitrate-N load vs. P relationship for winter-spring and total annual P are shown on Fig. 11. Figure 12 shows an interesting phenomenon - a negative correlation for maximum nitrate-N load and summer precipitation. Correlations are non-significant at $p<0.1$, but may indicate an effect of enhanced crop uptake of N on non-irrigated acreage with moderate rainfall. Conversely, increased nitrate-N load with less P may, in some circumstances, be caused by decreased denitrification when the water table drops below the solum and its supply of organic carbon (Starr and Gillham, 1993). Both causes are speculative.

Table 5. Pearson Product-Moment cross correlations for precipitation (P) and potential evapotranspiration (PET) parameters described in Table 3. Yellow = significant difference at $p<0.05$, green = significant difference at $p<0.1$.

	P-W	P-W-5	P-S	P-S-5	P-T	P-T-5
PET-W	-0.665	-0.712	0.255	0.230	-0.148	-0.443
PET-W-5	-0.774	-0.963	0.209	0.064	-0.237	-0.727
PET-S	-0.265	-0.193	-0.334	-0.330	-0.380	-0.321
PET-S-5	-0.711	-0.711	-0.334	-0.613	-0.606	-0.875
PET-T	-0.719	-0.703	-0.040	-0.058	-0.393	-0.584
PET-T-5	-0.830	-0.974	0.047	-0.157	-0.385	-0.849

Discussion

The data demonstrate a clear relationship between composite nitrate-N loads in the Englevale aquifer and climatic patterns, particularly winter and spring precipitation. The 1996 data indicate peak nitrate-N values in 1996, but the monitoring well network was incomplete at that time, and the specific well set may have biased the load estimates upward. It seems reasonable to assume that they were large, but how large relative to post-1996 measurements is difficult to ascertain. It is suspected that nitrate leaching in the Englevale aquifer was greatly enhanced by climatic shifts toward greater moisture in the early 1990s, as shown by increasing P trends on Figure 8. Similar large increases in nitrate-N were observed in other aquifers, notably the Karlsruhe aquifer (restricted report). But limited well networks prior to that time, and in some cases increased irrigation development, make it difficult to evaluate pre-existing nitrate conditions.

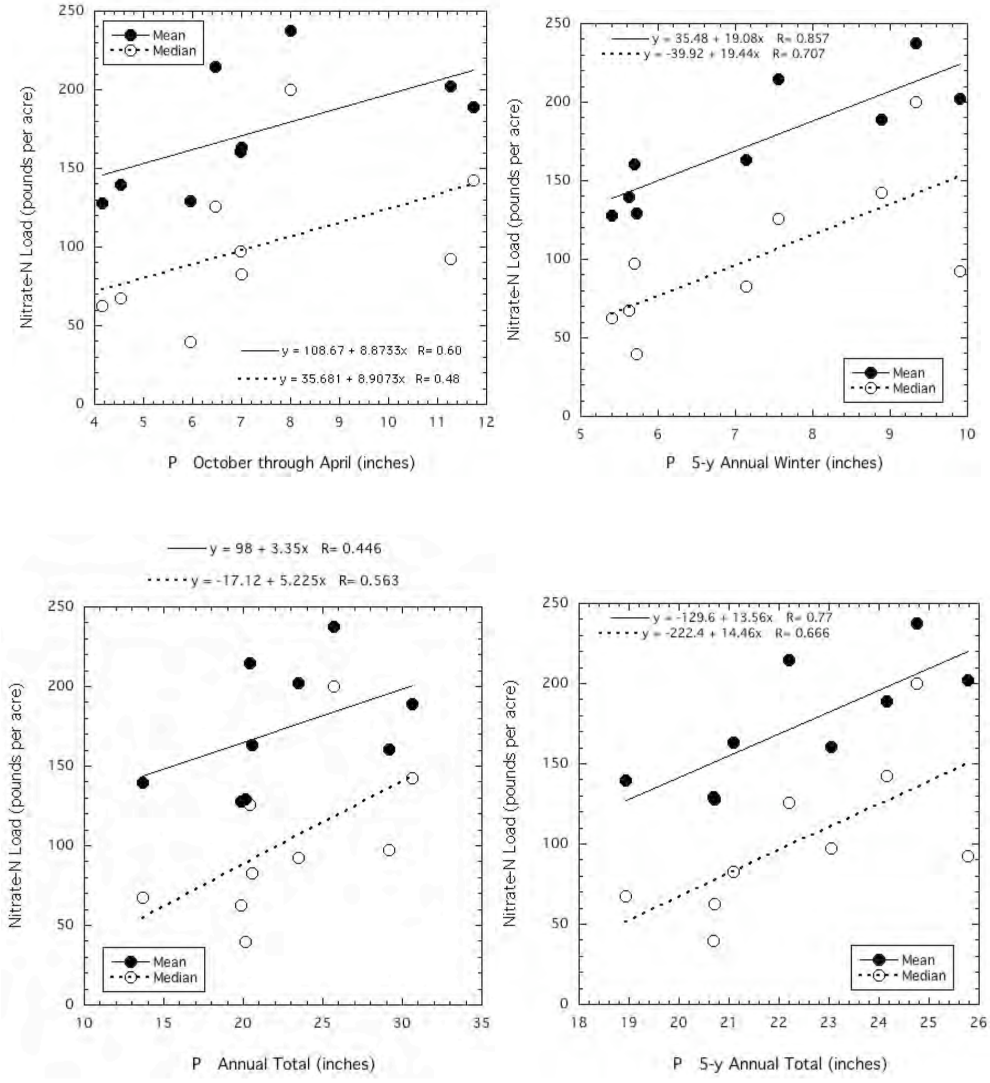

Figure 11. Relationship and correlation between mean and median nitrate-N load values and precipitation parameters (October through April, five-year average October through April, Total Annual, and five-year average Total P).

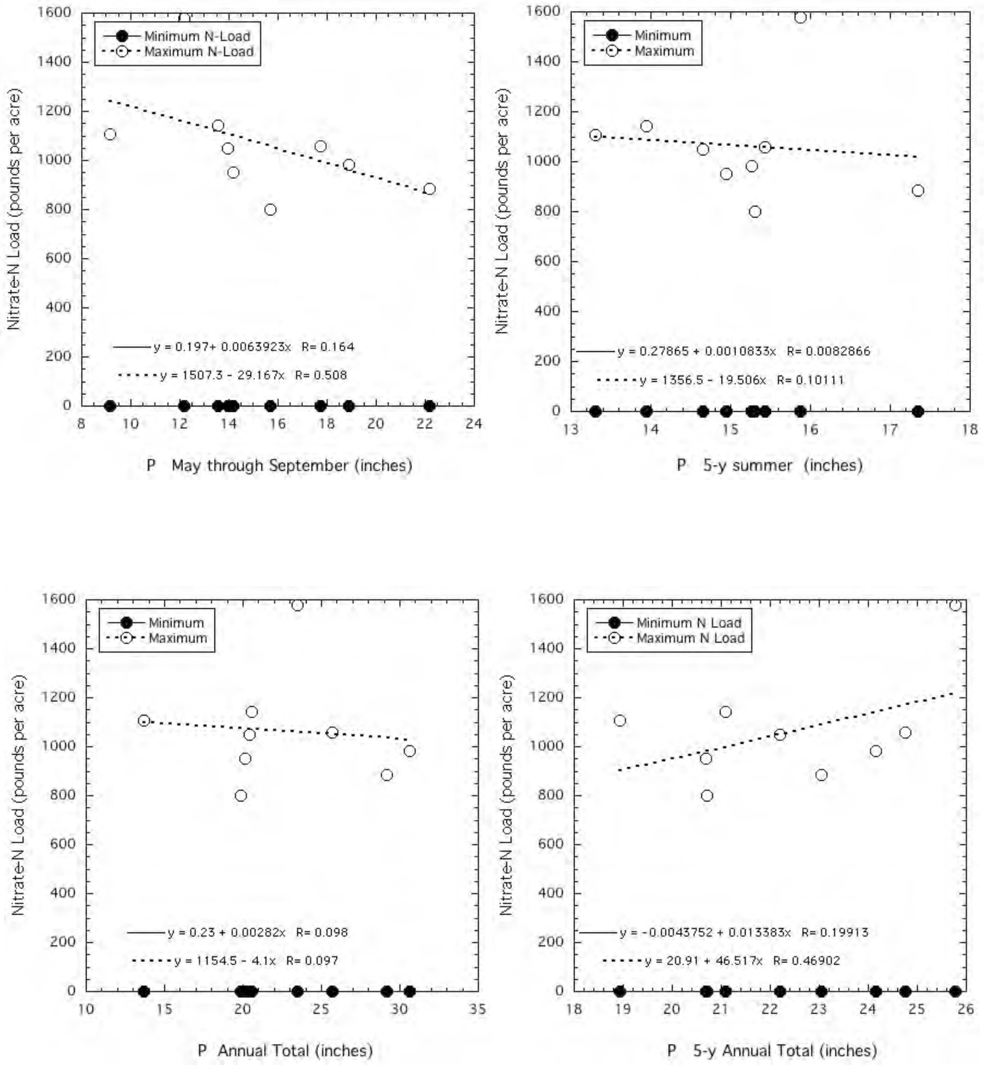

Figure 12. Relationship and correlation between minimum and maximum nitrate-N load values and selected precipitation parameters (May through September, five-year average May through September, Total Annual, and five-year average Total P).

One study - in the Carrington aquifer, a shallow confined aquifer - included measurements that began in 1992, prior to large precipitation in 1993 (Schuh and others 2004). Systematic upward shifts of 3-to 5x initial nitrate concentrations were observed in the saturated till pore water from 1993 through 1995. After 1995 nitrate began to trend downward in 1996. We suspect that similar processes, with some alteration for local rainfall events, occurred in other aquifers in the state. Data for the Englevale aquifer are consistent with these trends.

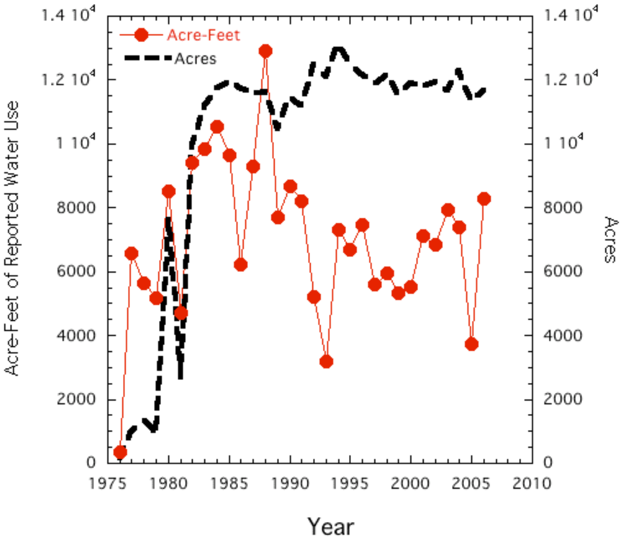

Figure 13. Irrigation water use trends for the Englevale aquifer.

Effects of Water Use on Nitrate-N Loads

One important potential source of increased nitrate leaching would be increased intensive high-value and irrigated agriculture. Irrigated acreage and water use trends, as indicated by irrigated acreage having points of diversion in the Englevale aquifer, are shown on Fig. 13. The main push for irrigation development occurred between 1976 and 1984, during which irrigated acreage increased from 160 acres to 11,733 acres. It remained approximately constant, and then, following the drought year in 1988, increased about 12% to 13,116 acres between 1988 and 1994. Most of the increased acreage was south of the study area of this report. Actual reported water use, however, varied inversely with P, with decreased water use in 1986 (a wet year), maximum water use in 1988 (a dry year), and minimal water use in 1993 (a very wet year) and 2005. There are no apparent trends in water use that correspond to or explain nitrate-N loads from the period of measurement (1997 through 2006). Regression analyses for nitrate-N load vs. irrigated water use were non-significant, and multiple regression models using varying P variables and irrigation water use exhibited no improvement over P variables alone. The primary variables affecting nitrate-N load values are climatic, and are not related to irrigation rates. While water use may not be significantly correlated, there may have been a relationship between aquifer nitrate and high-value irrigated agricultural practices during the transitional period of the early 1980s.

Effects of Local Well and Water-Table Characteristics on Nitrate and Sulfate

General relationships between the total nitrate-N load, sulfate-S load, nitrate-N concentration in the shallowest well on each site, and site hydrologic and well characteristics for all data, including all well sites and all sample dates are shown on Table 6.

Table 6. Correlation matrix for nitrate and sulfate indicators, and site hydrologic characteristics (N=415).

	Nitrate-N load	S-load	Shallow Nitrate
Nitrate-N load	1.000		
S-load	-0.027	1.000	
Shallow Nitrate Conc.	0.696	-0.122	1.000
H above well screen	0.030	-0.042	0.004
Top of Well Screen	0.266	-0.340	0.173
Saturated Thickness	0.046	0.236	0.066
WT Depth	0.360	0.474	0.198

Pearson Product-Moment correlation (Table 6) indicated a strong correlation for total integrated nitrate-N with depth only with shallow nitrate (as nitrate). The direct-regression relationship with total nitrate-N load accounted for 72% of all variability using a power function of nitrate alone (Fig. 14 below). This relationship should be useful as a rough approximation where shallow wells are not supplemented with deeper wells.

All other significant correlations were weak and accounted for very little of the total variability. Shallow nitrate concentrations were negatively correlated with total sulfate load ($p<0.05$). Total nitrate-N load was significantly (and positively) correlated with depth to the top of the (shallowest) well screen and with water table depth, which indicates that sites with deeper water tables were receiving and/or retaining more nitrate-N. This may have been caused by decreased denitrification when the water table dropped below the organic carbon source in the solum (Starr and Gillham 1993). There was no significant correlation of nitrate-N load or sulfate-S load with the saturated thickness of the aquifer. During 1997 and 1998 seasonal data were collected, with multiple sampling dates between June and November. There was no significant difference ($p<0.05$) in nitrate-N load or in shallow well nitrate concentrations between seasonal sampling periods (not shown).

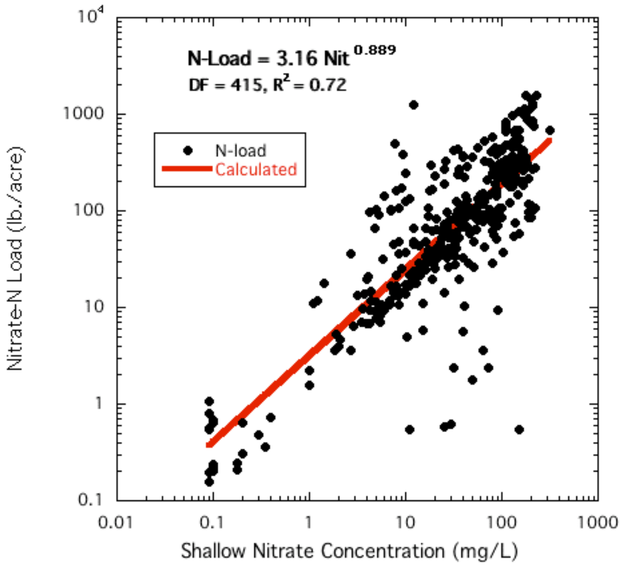

Figure 14. Total nitrate-N load and nitrate concentration in the shallowest well for each measurement on each well site.

Overview of Nitrate Contamination in Irrigation Wells

Nitrate data from 45 irrigation wells were used to evaluate nitrate contamination. Initial concerns over nitrate contamination were based on elevated measurements in water samples from irrigation wells beginning in 1996. Nitrate-N loads for irrigation wells were estimated by applying the multiple of the well-screen interval times the nitrate concentration for Eq. 2, and applying Eq. 3 and 4. For toxicological assessment of irrigation wells we simply use the nitrate-N concentration, assuming that the sample is a mixed representation of the local aquifer. It is analogous to the PMCI, and for sake of discussion we will label it a "Mixed Concentration Index," or MCI.

Results for nitrate-N loads (Fig. 15) show the large change in the distribution that occurred in 1996 water samples, prompting this investigation. Median nitrate-N loads approximately tripled from 0.23 lb./ac. (108 samples) for composite data before 1996 to 0.59 (106 samples) from 1996 through 2001. Three features of this data set are important for understanding its use in evaluating nitrate trends: (1) It extends only through 2001, and therefore cannot be used to evaluate dissipation trends. (2) It includes data that precedes the observation well set, which was mostly constructed in 1996 and 1997, and therefore is more useful for evaluating relative contaminant status before 1996. The data does generally confirm that a large change occurred. (3) Missing data in 1992, 1993 and 1994 limit the precision for identifying the relationship between initial elevated nitrate and the specific causal climatic events. However, the large change does occur after the post-1992 climatic shift.

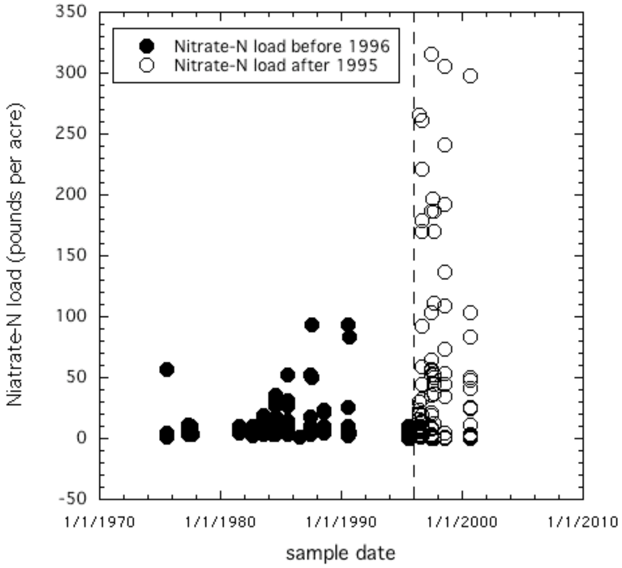

Figure 15. Nitrate-N loads for irrigation wells in the Englevale aquifer.

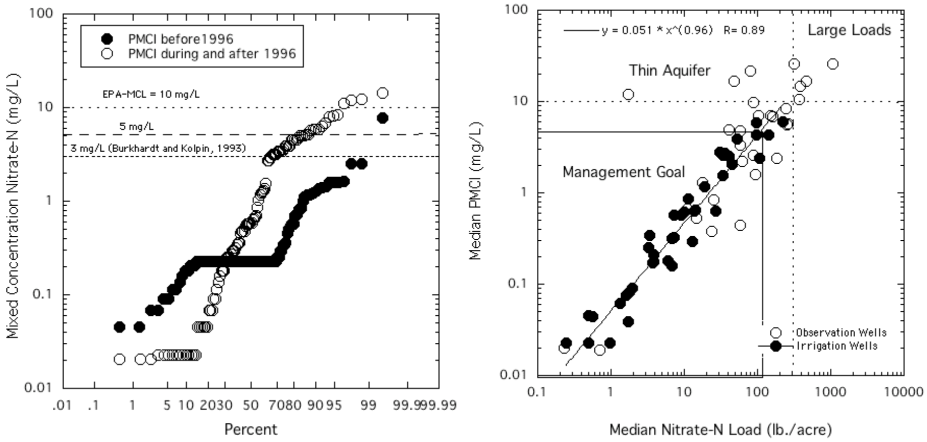

Figure 16. Comparison of probability distributions for pre- and post-1996 nitrate-N mixed concentrations in irrigation wells (left); and comparison of the relationship between toxicological standards and nitrate-N loading rates for irrigation wells and observation wells (right).

The probability distribution for pre- and post-1996 mixed concentrations (Fig. 16) shows that before 1996 none of the well samples exceeded the EPA-MCL, and all but one were less than 3 mg/L nitrate-N. From 1996 through 2001 65% were less than 3 mg/L, 80% less than 5 mg/L, and 4% were above the EPA-MCL (10 mg/L).

Median mixed nitrate-N concentrations vs. nitrate-N load for the post-1995 irrigation-well water samples (Fig. 16) follow an identical power function as that derived for the median post-1995 observation well data (Fig. 6 and Fig. 16), which was used to derive the interpretive matrix used to evaluate nitrate contamination status (Table 2). The same matrix is thus used to evaluate the irrigation well data. All median values for irrigation wells are below the "high" class (>EPA-MCL), and almost all median load values are below a low one-year crop equivalent load of about 100 lb./ac. Generally lower mixed concentrations and loads for the irrigation wells would be expected because of: (1) broader areal representation caused by actual (vs. theoretical) mixing which dampens local variability; (2) nitrate extraction through pumping wells which would tend to prevent local accumulations of nitrate near the wells; and (3) location of well-screen intervals of some of the wells in the lower aquifer unit.

Causes of Nitrate-N Dissipation in the Englevale Aquifer

Changes in measured nitrate concentrations within an aquifer can occur only through: (1) decreased nitrate input; (2) discharge to the root zone with subsequent plant uptake; (3) discharge to rivers, streams and wetlands; (4) dilution through dispersion; and (5) microbial denitrification or non-assimilative nitrate reduction (Korom, 1992). Dilution affects only local concentrations and does not constitute removal, since it merely represents spreading to other portions of the aquifer. Dilution should not affect the total nitrate-N load in the aquifer. Non-assimilative nitrate reduction represents what may be a temporary transformation to ammonium, and may reoxidize to nitrate under oxidizing conditions.

Average nitrate-N concentrations in the Englevale aquifer have been shown to be gradually decreasing at a rate of about 4 to 8% per year. In this section we will examine the plausibility of denitrification contributing to the measured average decrease in nitrate-N load.

During the late 1980s and early 1990s, research in northern Europe (Kolle and others 1985, Mariotti 1986, Postma and others 1991) and in the United States (Korom 1992, Puckett and others 2002, Tesoriero and others 2000) and Canada (Phipps and Betcher 2003) indicated that variable portions of nitrate could be removed from ground water through denitrification which converts and releases nitrate as N_2 gas. Denitrification is usually accomplished by heterotrophic microbes which use carbon as an electron donor, through a reaction expressed stoichiometrically in the generic equation:

$4NO_3^- + 5/6\ C_6H_{12}O_6 + 5\ CaCO_3 + 4H^+ = 2N_2 + 10\ HCO_3^- + 5Ca^{2+} + 2H_2O \qquad (6)$

Or by chemoautotrophic bacteria which remove nitrate using inorganic sulfur and/or iron from pyrite or other minerals as electron donors through a reaction exemplified stoichiometrically in the generic equation for pyrite:

$$5\ FeS_2 + 14\ NO_3^- + 4\ H^+ = 7\ N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O \qquad (7)$$

Many of North Dakota's Cretaceous bedrock formations, including the Carlile, Niobrara, and some members of the Pierre Formation contain relatively plentiful pyrite, which formed in an anaerobic high-organic sea-bottom environment during the process of sedimentation. Sand grains composed of shale in glacial aquifers formed from the detritus of glacial action frequently contain some amount of pyrite which can be used to chemically denitrify (Schuh, Bottrell and Korom 2006).

The Elk Valley aquifer was the first North Dakota aquifer in which substantial denitrification was identified. Dr. Gale Mayer (Mayer 1992) observed inverse stratification of sulfate and nitrate and identified the presence of denitrifying bacteria in the upper aquifer. Patch and Padmanabhan (1994) used ^{15}N nitrate-N stratification in the Elk Valley aquifer to demonstrate the occurrence of denitrification.

Dr. Scott Korom and his students have subsequently conducted quantitative studies on denitrification in the Elk Valley aquifer and several others in North Dakota and Minnesota. In situ mesocosm (ISM) studies in the Elk Valley aquifer (Grand Forks County) indicated an "apparent zero-order denitrification rate" of 16 mM/d (0.22 mg/L/d) for denitrification of nitrate as N (Korom and others 2005). The main electron donors were identified as pyrite-S (58%), iron (<4%), and organic matter. A summary of denitrification studies in North Dakota and Minnesota yielded the following conclusions: In North Dakota, the Elk Valley aquifer [0,11-0.22 mg/L/d, source S,Fe(II),OC]; the Warwick aquifer (not active); the Kidder County aquifer (0.07 mg/L/d, likely Fe(II)); in Minnesota, the Shingobee River (0.07 mg/L/d, likely Fe), the Rock River (0.05 mg/L/d, Fe(II) likely), the first Otter Tail aquifer site (0.04 mg/L/d, S and possible Fe(II)), and the second Otter Tail aquifer site (0.06 mg/L/d, OC, possibly Fe), reported by Korom to the North Dakota Department of Health, dated August 7, 2002. Tesfay and Korom (2006) have conducted research to identify the specific role of FE(II) in denitrification, and concluded that "FE(II)-supported denitrification appears to have a significant role as a natural remediation process in the aquifers of our region."

Dr. Korom's students, Eben Spencer (2005) and Jason Warne (2002), conducted research on the Karlsruhe aquifer and determined that about half of the sites had significant denitrification. Additional ^{15}N data collected by the SWC from the Carrington aquifer in Foster County have indicated likely occurrence of denitrification in that aquifer (Schuh, unpublished data). Warne (2004) determined an approximate zero-order denitrification constant of 0.074 mg/L/d for one ISM in the Karlsruhe aquifer. At this rate, a nitrate-N concentration of 25 mg/L (approx. 2.5 x the EPA-MCL of 10 mg/L) would be fully denitrified within one year (333 d). However, Warne further indicated that a first order rate of the form:

$$C = C_o e^{-kt} \qquad (8)$$

and k = 0.0031/d provided a better model. If this were the case, the denitrification rate would be considerably enhanced, and a 100 mg/L initial nitrate-N concentration would undergo a concentration-dependent denitrification rate ranging initially from about 0.3 mg/L/d to about 0.1 mg/L/d after 365 days for C_o = 100 mg/L, and 0.077 to 0.025 mg/L/d for C_o = 25 mg/L. With this equation, any initial concentration would decrease approx. 68% over 365 days. The corresponding C (365 day) for C_o of 100 mg/L would be about 32 mg/L, and C_o of 25 would be about 8 mg/L.

Because microbial uptake and metabolism of nutrients frequently prefers lighter elemental species, the isotopic speciation of oxygen and nitrogen in dissolved nitrate can provide evidence of denitrification. Commonly, ^{15}N and ^{18}O isotopes are used to interpret denitrification trends and sources. Interpretation is based on: (1) knowledge of ^{15}N composition of fertilizer N; (2) knowledge of ^{18}O and ^{15}N changes resulting from microbial nitrification of ammonium N; (3) absolute and relative changes of ^{18}O and ^{15}N isotope composition during denitrification; and (4) knowledge of the flow system in which these changes are occurring. Additional evidence of autotrophic denitrification using reduced sulfide can be obtained from ^{18}O and ^{34}S composition of sulfate.

(1) With respect to the Englevale aquifer, almost all fertilizer-N currently used is in the ammonia/ammonium (NH_3/NH_4^+) form. Principal fertilizer-N sources are anhydrous ammonia (gaseous NH_3), which is produced from atmospheric N using the Claude-Haber process (p. 360, Tisdale and Nelson 1966); urea [$CO(NH_2)_2$], which is produced from gaseous ammonia and CO_2; and mon-ammonium- and di-ammonium-phosphate (MAP and DAP), both produced from gaseous ammonia. For purpose of cost, ammonium sulfate is also sometimes used in North Dakota irrigated agriculture. Because

all are derived from atmospheric N, the ^{15}N composition of the fertilizer sources is similar to atmospheric N (the standard) at $\delta^{15}N \sim 0$ o/oo.

(2) Almost all crop nitrate is taken up in the highly mobile nitrate form. Nitrate-N is produced by microbial nitrification of ammonium in the soil after application. Laboratory Research by Andersson and Hooper (1983) and Hollocher (1984) and reviewed by Spencer (2005) has indicated that following nitrification;

$$\text{Nitrate } \delta^{18}O = 2/3\ \ \delta^{18}O \text{ (local ground water)} + 1/3\ \ \delta^{18}O \text{ (local atmospheric } O_2\text{)} \quad (9)$$

(3) During denitrification, denitrifying bacteria preferentially respire lighter nitrate-N and nitrate-O, leaving a heavier residual in the dissolved fraction. The relative increase in dissolved nitrate ^{18}O occurs at about half the rate of ^{15}N (from Mengis and others 2001, and reviewed by Spencer, 2005).

(4) Because the lighter N is delivered to the aquifer in recharge waters from the surface, and because reducing conditions seldom occur in the upper recharge zone, heavier nitrate N ($>^{15}N$) and O ($>^{18}O$) would be expected with increasing depth under most conditions. Exceptions might be evaporative discharge zones sufficiently dominant to bring deeper waters to the surface or discharge wetlands having large organic matter pools which would cause heterotrophic denitrification within the discharge zone. Because fertilizer sources and nitrification have $\delta^{15}N$ signatures near to or lighter than 0 o/oo, and the $\delta^{15}N$ signature is substantially larger following denitrification, the likelihood of denitrification can be assessed independent of the flow system. The location of the heavier N would, conversely, serve as an indicator of the characteristics of the flow system with respect to nitrate.

Englevale Aquifer Isotopes

Six sites were selected for isotope samples. Sites were selected based on: (1) sufficiency of nitrate-N for extraction; (2) evidence of stratification; and (3) representation of different areas of the Englevale aquifer. Four sites were selected in the north, two each in Section 134-057-18 and Section 134-058-25; one in the middle of the aquifer (north to south) in Section 133-058-25, and one in the south in Section 132-058-35. Locations are shown on Fig. 17. Water samples were collected in November, 2006. Samples were frozen within 12 hours, and sent to the Environmental Isotope Laboratory at the University of Waterloo, Ontario, Canada. All samples were assayed for nitrate ^{15}N, sulfate ^{34}S, and ^{18}O in sulfate and nitrate. Two water samples were assayed for ^{18}O and deuterium (^{2}H) in water. These data are summarized on Table 7.

The source of nitrate-N in the Englevale vadose/ground-water system would be a mixture of soil organic-matter decomposition, fixed nitrogen from storms and *rhizobia (sp.)* bacteria on roots of leguminous crops (mainly edible beans) grown in the area and asymbiotic fixation, and nitrified ammonium-N from fertilizer. ^{15}N fractionation during these processes is complex and varied. Carol Kendall (2004), in a web-published overview of environmental N isotopes, has indicated that the usual effect of microbial fractionation is heavy isotope depletion in the product and enrichment in the residual substrate. Thus, nitrification would tend to cause depletion of nitrate-^{15}N (the reaction product), but denitrification would tend to enrich nitrate-^{15}N (residual substrate). Middelburg and others (1996), fixation of nitrate has little effect on ^{15}N fractionation (+/1 to 2 ‰). General ranges of δ^{15}N in nitrified ammonium fertilizer provided by Kendall (2004) are in the range of 0 to -5 o/oo, while nitrified soil ammonium-N is in the range of +5 to +10 o/oo. The predominant soil δ^{15}N product overlying the Englevale aquifer would thus be expected to be influenced mainly by the nitrified fertilizer fraction, with some upward modification caused by the contribution of nitrified soil N. The least enriched δ^{15}N for the Englevale aquifer nitrate data are approximately +4 o/oo, which is consistent with this expectation. It will be seen that these correspond to the shallowest wells.

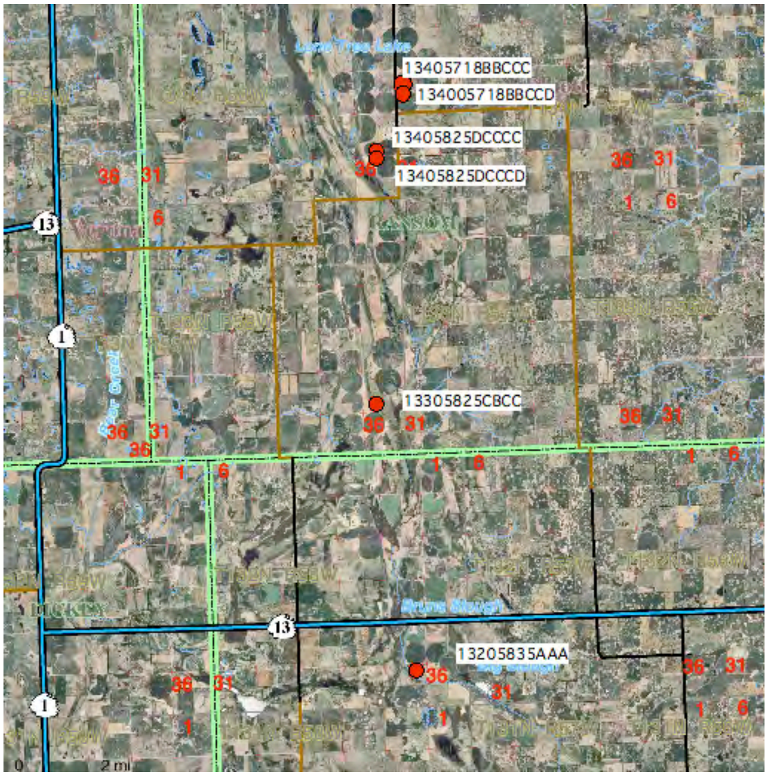

Figure 17. Map of locations for isotope samples.

Table 7. Results of isotopic analysis for nitrate ^{15}N, sulfate ^{34}S, ^{2}H in water, and ^{18}O for nitrate, sulfate and water.

Sample	(1) $^{18}O/H_2O$	(1a) Repeat	(2) $^{2}H/H_2O$	(2a) Repeat	(3) $^{34}S/SO_4$	(3a) Repeat	((4) $^{18}O/SO_4$	(4a) Repeat	(5) $^{18}O/NO_3$	(5a) Repeat	(6) $^{15}N/NO_3$	(6a) Repeat
	o/oo SMOW	o/oo SMOW	o/oo SMOW	o/oo SMOW	o/oo CDT*	o/oo CDT*	o/oo SMOW*	o/oo SMOW*	o/oo SMOW	o/oo SMOW	o/oo SMAN	o/oo SMAN
13205835AAA9					-7.99		-4.19	-4.17	3.95	3.44		8.05
13305825CBCC3					-6.81							7.37
13305825CBCC4					-5.99		-2.63	-2.62	1.86			5.3
13405718BBCCC2					-6.82		-5.28		10.38	10.08		23.27
13405718BBCCC3					-6.31	-6.31						3.88
13405718BBCCD1	-12.37		-90.99	-91.21	-7	-7.28	-4.93				-0.416	
13405718BBCCD2					-6.67		-5.24	-5.43	6.21	5.87		14.17
13405718BBCCD3	-10.5		-76.78	-76.36	-6.6						0.83	3.76
13405825DCCCC2					-7.9		-4.84	-4.07	15.52	15.84		36.31
13405825DCCCC4	-9.85		-69.24	-68.94	-5.39		-4.45	-4.21	1.62		1.26	4.99
13405825DCCCD1					-7.74							8.09
13405825DCCCD2					-7.06							4.78
13405825DCCCD3	-11.63	-11.81	-85.12	-84.64	-7.05	-7.06	-5.64	-6.28	1.45	1.84	0.077	4.42

SMOW = Standard mean oceanic water, CDT = Canyon Diablo Troilite standard, SMAN = Standard mean atmospheric N.

Applying Eq. 9 to $\delta^{18}O$ for local water samples (Table 7, column 1) and an estimated $\delta^{18}O$ of +23.5 ‰ for atmospheric O_2 (from Phipps and Betcher, 2003) gives a mean estimated nitrate-N $\delta^{18}O$ of 0.442 ‰ +/- 1.2 at $p < 0.05$. $\delta^{18}O$ corresponding to $\delta^{15}N < +5$ ‰ are + 1.62 ‰ and + 1.45 ‰. These compare with corresponding calculated values of +1.26 ‰ and +0.077 ‰ respectively (Table 7, column 5b). The statistical distribution of $\delta^{18}O$ and the corresponding estimates for nitrate-^{18}O, assuming nitrification, is shown on Table 8.

Table 8. Statistical description of ^{18}O for Elk Valley aquifer water samples, and corresponding ^{18}O for expected nitrate values calculated using Eq. 9.

	$\delta^{18}O/H_2O$ o/oo SMOW	Calculated (Eq. 9) $\delta^{18}O/NO_3$ o/oo SMOW
Minimum	-12.37	-0.416
Maximum	-9.85	1.264
Points	4	4
Mean	-11.088	0.439
Median	-11.065	0.454
Std Deviation	1.128	0.752
Std Error	0.564	0.376

Both ^{15}N and ^{18}O data for minimum measured values from aquifer samples are within a reasonable expected range for nitrified N from ammonium-based fertilizers. Since residual nitrate-N in ground water are enriched in both ^{15}N and ^{18}O during denitrification, both should increase proportionately with denitrification. The expected relative rate of increase is: $\delta^{18}O / \delta^{15}N = 0.5$ (Mengis and others, 2001). Increasing ^{18}O is highly correlated ($r>0.99$) with ^{15}N for all of the Fall 2006 Englevale isotope data (Fig. 18), with a regression coefficient of 0.485. There is no significant difference of the coefficient difference from 0.5 for any coefficient > 0.41 at $p<0.05$. The relationship thus corresponds almost exactly to the expectation for denitrification processes.

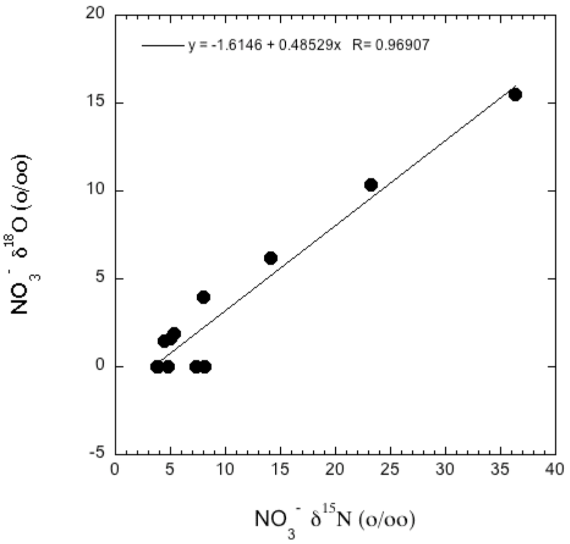

Figure 18. Composite ^{18}O vs. ^{15}N data for Englevale Fall 2006 water samples.

Figure 19 shows composite of ^{18}O and ^{15}N vs. sample depth below the water table. Results show consistent, similar, and highly correlated exponential increases in both isotopes with depth. The consistency of the relationship indicates a similarity between sites of hydrologic processes controlling solute transport. The close composite relationship is consistent with a similar general source-sink behavior over a broad area of the aquifer, encompassing more than 14 linear miles in the north-south direction. Lowest enrichment at shallowest depth indicate that the "freshest" nitrate is entering at the surface through leaching. Exponential increases with depth are consistent with denitrification along a flow path in which nitrate is progressing with depth in the flow system, moving into increasingly unoxidized layers.

All of the sites are located on seasonal recharge areas (Table 9), with little evaporative discharge. The depth to the water table, measured in October of 2006, is greater than 17 feet for all sites, and therefore uncoupled with respect to evapotranspiration. Shallowest wells on all sites are relatively low with respect to sulfate concentrations, so gypsum is not present in the upper aquifer, and is unlikely to be present in the soil as a leaching source, since solid gypsum stability requires an EC > 4 dS/m (Steinwand and Richardson 1989). All sites have relatively low total dissolved solids (TDS) concentrations in the shallow well water, again indicating no evaporative concentration. All of the sites are mapped to soils classified in the Hapludoll great-group taxa. These have been described as seasonal recharge areas (Seelig and Richardson, 1994). Site 132-058-35AAA is located within an area in which Calciaquoll soils constitute a secondary mapping unit. However, TDS, sulfate and water table depths measured at the well site (Table 1) indicate that the Gardena series (Hapludoll) may be the more appropriate classification for the well site.

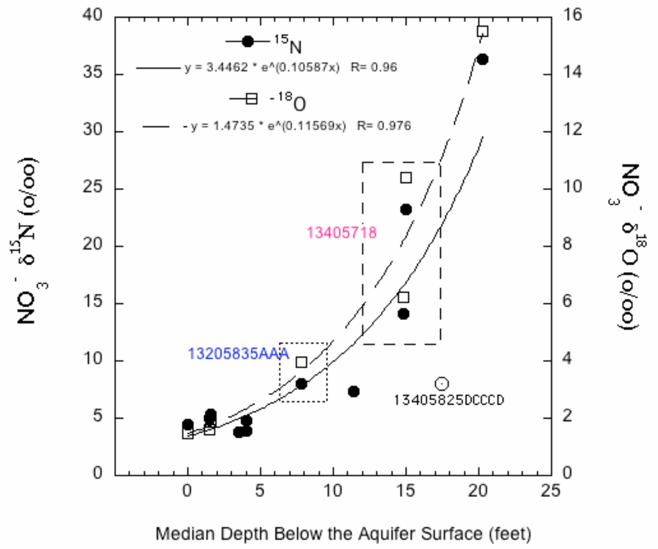

Figure 19. Composite ^{18}O vs. and ^{15}N data vs. depth below the water table for Englevale Fall 2006 water samples.

These similar site characteristics support, and partially explain the consistency of the ^{15}N and ^{18}O data vs. depth relationship. There are other conceivable hydrologic settings in which this relationship would likely not hold. For example, a discharge site, either evaporative or flowing, might contain heavier ^{15}N and ^{18}O caused by denitrification earlier in the flow path and transported to the discharge zone. Tesoriero and others (2000) and and Puckett and others (2002) have described the progression of ^{15}N along ground-water flow paths. Similarly, soils in discharge zones could be enriched with ^{15}N due to higher organic matter and colder and wetter conditions. For example, Karamanos and others (1981) have reported higher natural ^{15}N values in soil near saline seeps. Kendall (2004) speculated that ^{15}N enrichment in this case could be caused by local denitrification. For a shallow water table located in a local depressional area, with higher soil organic matter from erosion and retention under cool-wet conditions, local denitrification would possibly be enhanced. Under such conditions ^{15}N of shallow ground water could be enriched following periodic flushing from recharge events.

Table 9. Soil classification and shallow chemical data related to local recharge status.

Location	WT depth Feet	TDS mg/L	SO4 mg/L	Soil Series (mapping unit)	Great-Group
13405825DCCCD	19.12	626	160	Brantford-Coe	Hapludoll-Hapludoll
13405825DCCCC	20.43	763	166	Brantford-Coe	Hapludoll-Hapludoll
13205835AAA	17.6	528	76.6	Gardena-Glyndon	Hapludoll-Calciaquoll
13305825CBCC	18.84	880	252	Sioux-Renshaw	Hapludoll-Hapludoll
13405718BBCCC	18.88	578	137	Renshaw-Sioux	Hapludoll-Hapludoll
13405718BBCCD	21.8	613	142	Sioux-Renshaw	Hapludoll-Hapludoll

The relative change in nitrate concentration with relative change in isotopic enrichment, with reference to the maximum nitrate concentration and corresponding $\delta^{15}N$ for each site, can be described approximately as a power function for the composite data (Fig. 20). Because the coefficient of the power function is very close to 1, and the exponent is close to 0.5, we might suggest, as a simple approximation for the composite data, that the relative nitrate dissipation through denitrification varies approximately with the square root of the relative $\delta^{15}N$ isotopic enrichment.

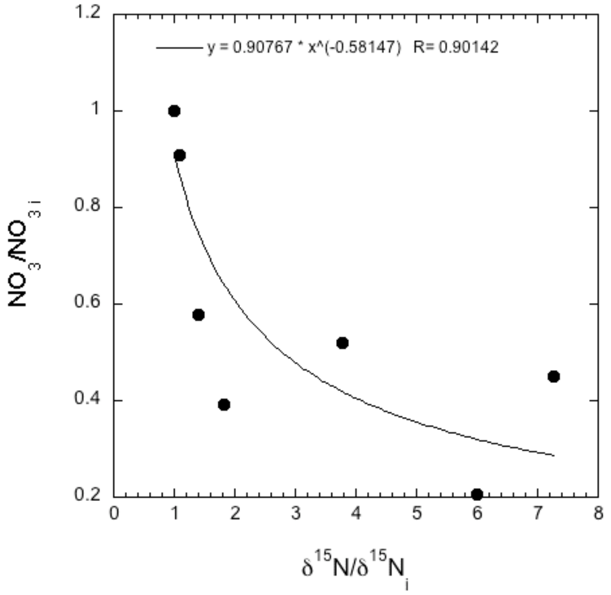

Figure 20. Relative change in nitrate concentration vs. corresponding relative change in isotopic enrichment.

Stratified nitrate (Fig. 21) on all of the isotope collection sites supports the conclusion of denitrification. However, neither stratified nitrate nor ^{15}N data identifies the electron donor. The grain matrix of the Elk Valley aquifer includes a substantial amount of shale in the sand fraction, as indicated by mechanical weathering when using a dry auger. Drilling logs have indicated shale-sand composition as high as 50 to 70%. Many shale bedrock materials in North Dakota contain pyrite (Schuh, Bottrell and Korom 2006) and some aquifers, like the Elk Valley aquifer (Korom and others 2005) have been shown to have large denitrification using pyrite sulfur and iron as an electron donor. Others (Korom, report to the North Dakota Department of Health, dated August 7, 2002, Warne 2002, Spencer 2005) have reduced iron or organic carbon as electron donors. Inverse stratification of sulfate on three of the isotope sample sites (Figure 18) indicates that sulfur, possibly from pyrite in the shale fraction, may contribute to denitrification in the Englevale aquifer. However, non-stratified sulfate on half of the sample sites indicates that other processes, possibly other electron donors, or other hydrologic processes such as recent recharge, may be occurring.

^{34}S isotope data for dissolved sulfate (Table 7) indicates a likely mixed sulfate source. Pyrite in high-organic shale usually has very low ^{34}S enrichment due to microbial exclusion in the process of sulfur reduction during the sedimentation. Shale pyrite $\delta^{34}S$ for various bedrock sources in North Dakota have median values ranging from approx. -16 to -38 ‰ CDT (Bottrell's data, from Tables 3 and 4 in Schuh, Bottrell and Korom 2006). Porewater sulfate derived from pyrite in the Elk Valley aquifer had $\delta^{34}S$ ranging from approx. -15 to -30 ‰ CDT. $\delta^{34}S$ for all of the dissolved sulfate in the Englevale aquifer samples were consistent between approx. -5 and -8 ‰. Three fertilizer sulfate samples (ammonium-sulfate) ranged from -4 to +10 ‰ , sulfate in precipitation (snow) was slightly positive (+1.5 ‰), and topsoil sulfate was -1.1 and +2.1 ‰ in two samples. The consistent and relatively tight range of $\delta^{34}S$ between -5 and -8 ‰ in the Englevale aquifer dissolved sulfate indicates a mixture of sulfur from fertilizer, topsoil and precipitation sulfate sources and in situ oxidation of pyrite. Some contribution from oxidation of reduced mineral S would be required to achieve the dissolved sulfate values measured in the Englevale aquifer.

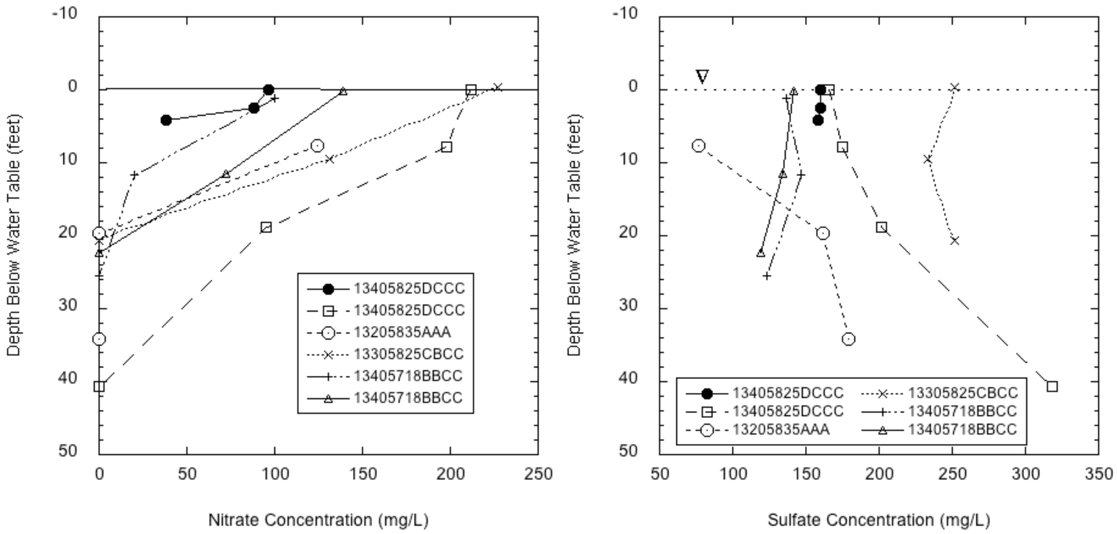

Figure 21. Depth (bwt) profiles for nitrate (as nitrate) concentrations (left), and sulfate (right) on Englevale aquifer sites sampled for isotope analysis.

^{34}S data indicating local pyrite oxidation do not necessarily confirm denitrification using sulfur as an electron donor (Eq. 2), as pyrite can be chemically and microbially oxidized in the presence of oxygen, as exemplified by:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 4H^+ \qquad (10)$$

or in the presence of water and iron(III):

$$14Fe^{3+} + FeS_2 + 7O_2 + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (11)$$

which incorporates oxygen molecules into sulfate from ground water without isotopic fractionation (Lloyd 1967, Toran and Harris 1989, McCarthy and others 1998). Equation 10 would have the largest contribution of O_2 from atmospheric oxygen having a highly enriched δ^{18}O of +23 ‰ SMOW. For the Englevale water data we would expect sulfate ^{18}O to have an enrichment of approx. +15 to +16 ‰ SMOW. Sulfate oxidation during denitrification (Eq. 2) would yield sulfate δ^{18}O similar to nitrate at approx. +1 to +2 ‰ SMOW (for the Englevale data). Sulfate oxidized from pyrite via Eq. 6 would have δ^{18}O similar to water at approx. -10 to -13 ‰ (for the Englevale data). Given the variability of ^{18}O sources having enrichment greater than local measured sulfate values, autotrophic denitrification using pyrite as an electron donor can neither be confirmed nor excluded using ^{18}O data. However the ^{18}O data suggest a contribution from water and iron(III)-based oxidation of pyrite (Eq. 11) to the overall sulfate pool.

In Summary, ^{15}N and ^{18}O data for dissolved nitrate indicate that denitrification is occurring at all of the six sites for which water samples were collected. Isotope results are consistent with a predominant nitrified ammonium-based N source, aquifer entry through leaching to the surface, and progressive denitrification with depth as nitrate enters the unoxidized zone. All sites combined exhibited a coherent exponential isotope vs. depth relationship for both ^{15}N and ^{18}O, and an approximate power function for relative ^{15}N enrichment vs. relative nitrate concentrations. The consistency of the depth relationship likely depends on the similarity of local hydrology (seasonal recharge areas) on all measured sites. ^{34}S and ^{18}O isotopic signatures for dissolved sulfate were consistent with denitrification using a pyrite-sulfur source as an electron donor, but were nonconclusive and indicated that many sulfur sources and oxidizing processes were likely affecting local sulfate concentrations. Nitrate stratification (decreasing with depth) is consistent with the evidence of denitrification. Inverse sulfate concentration profiles (increasing with depth) on some sites support the likelihood of autotrophic denitrification on at least some of the sites. We conclude that denitrification is occurring. Maximum overall rates would be 4 to 8 %, and electron donors are speculative and likely varied, but almost certainly include reduced sulfur and iron to some degree.

OBSERVATION WELL-SITE ANALYSIS

The Englevale aquifer lies predominantly within Townships 131 through 135, Ranges 57 and 58 in Ransom and Sargent Counties, North Dakota. This report is concerned primarily with portions of the aquifer bounded on the north by State Highway 27, and on the south by State Highway 13.

In this section we examine the characteristics of nitrate loads, and loading trends for individual monitoring-well locations and sites, and local factors affecting those trends. The analysis is presented in three general site groupings: (1) The north Englevale aquifer, including Township 134 N, Range 57 W and Township 134 N, Range 58 W wells; (2) the middle Englevale aquifer (Township 133 N, Range 58 W wells), and (3) the south Englevale aquifer (Township 132 N, Range 58 W wells). The discussion proceeds from north to south. While there are stratigraphic and hydrologic differences in the aquifer from north to south, the groupings are made primarily for the purpose of organization, and are not delineated on the basis of hydrologic properties. For each group there is (are) one or two (in the north) principal land section(s) which is (are) more heavily instrumented and monitored, and an ancillary group of single measurement sites in other sections.

North Englevale Aquifer (Township 134 N, Range 57 W and Range 58 W)

The northern portion of the Englevale aquifer is divided into two principal flow systems, which are separated by an elevated component of the underlying till aquitard. The till divide approximately bisects the western halves of Sections 18 and 19 (Township 134 N, Range 57 W) and the western halves of Sections 24 and 25 (Township 134 N, Range 58 W) along a north-south axis (Fig. 2). A generalized cross section of the northern Englevale aquifer is shown on Fig. 22. While the flow systems are connected across the divide in some areas (the aquifer has a saturated thickness of about 20 feet at 134-057-18CCC), and while some east-west flow would be supported by approximately 10 ft. of head differential from east to west across the divide where connected, the predominant flow direction on each side of the divide is from north to south (Fig. 2).

Fig. 23 shows a composite east-west stratigraphic transect across Sections 18 (Range 57 W) and Sections 13 and 14 (Range 58 W), with some inclusion of the south boundary of Sections 10 and 11 (Range 58 W). The transect shows the transition from the eastern channel (134-057-20ABB to -18CCC), through the thinner divide (-18DDD to -18CCC), to the deeper western channel (-18CCC to 134-058-23AAA). A total of 27 irrigation wells are located within the boundaries of Township 134 N, Ranges 57 and 58 W. Of these, 13 are located along the western boundaries of Sections 7, 18, and 19

(Range 57 W) and along the eastern boundary of Section 13 (Range 58 W). The rest are distributed in Sections 1 and 24 (Range 58), and in western half of Section 18 of Range 57 W.

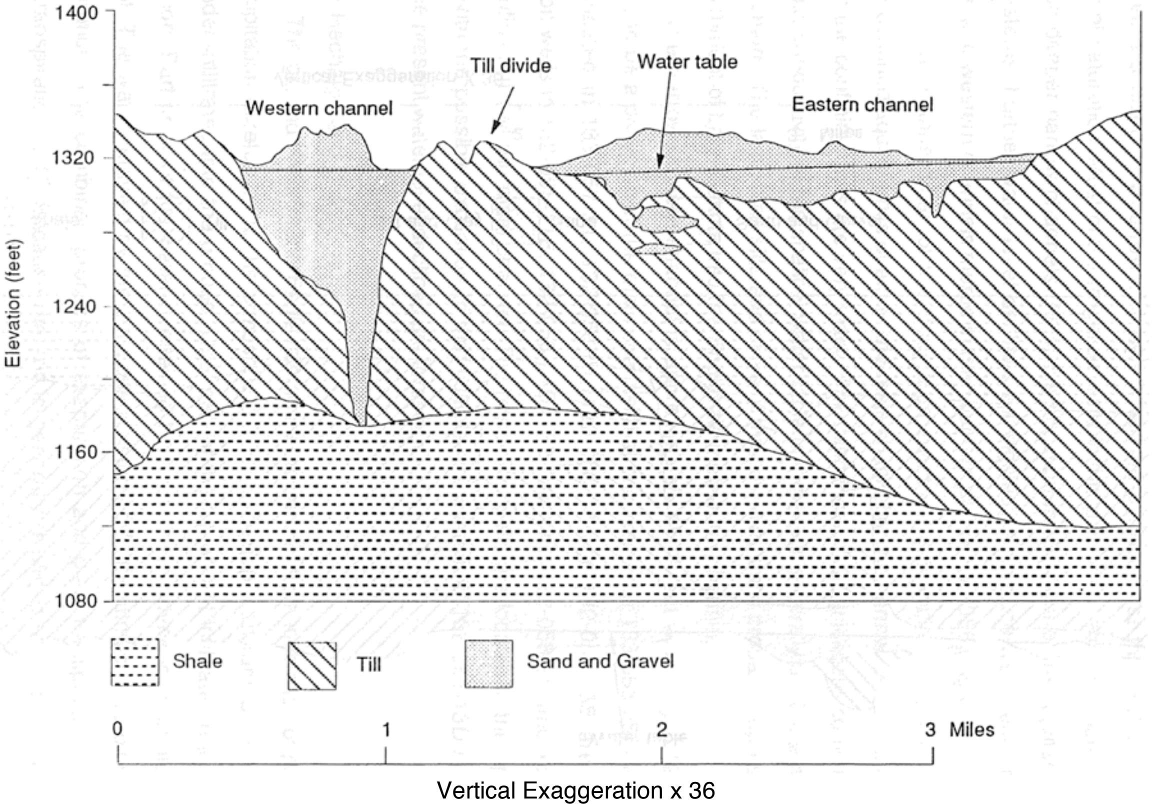

Fig. 22. Generalized cross-section of the northern Englevale aquifer (From Cline and others 1993).

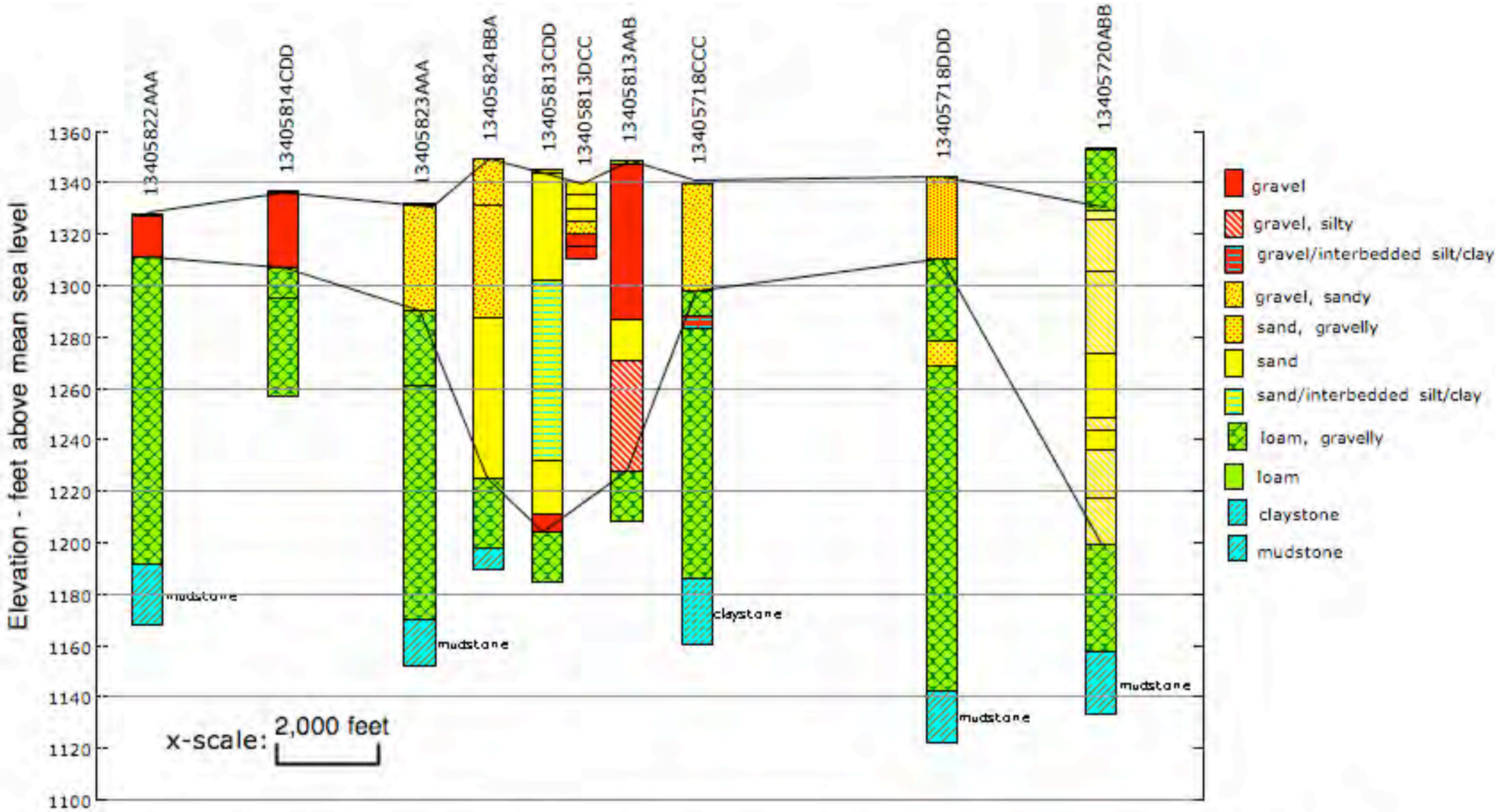

Figure 23. Englevale aquifer stratigraphy transect for the North Englevale aquifer (Township 134 N, Ranges 57 W and 58 W: USBLM 134-057. 134-058).

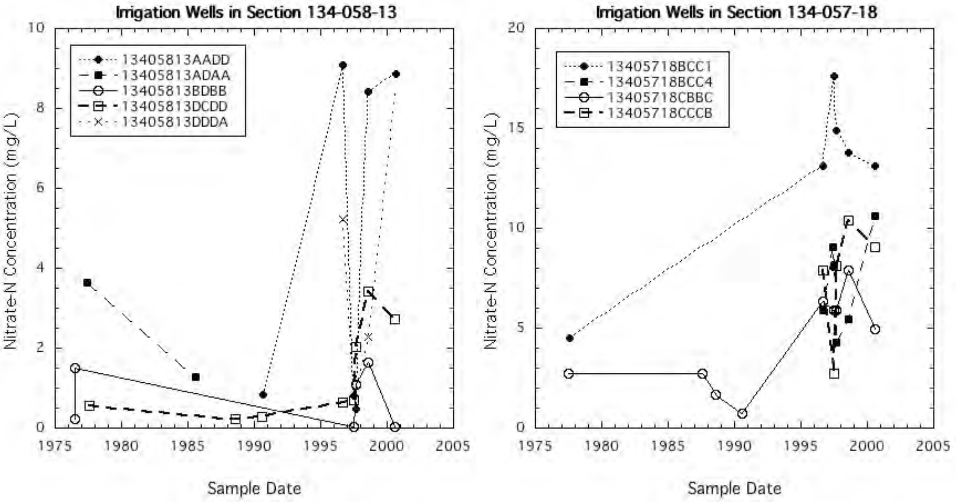

Fig. 24. Temporal variation of nitrate-N concentrations for selected irrigation wells in Sections 134-057-18 and 134-058-13.

Nitrate-N concentrations for four irrigation wells in 134-057-18 and five irrigation wells in 134-058-13 are shown on Fig. 24. All wells except one (134-058-13BDBB) exhibited increased nitrate during the mid 1990s. Large-scale leaching of nitrate following large rains during and after 1993 was a likely cause. There was a general progression of decreasing nitrate-N concentrations from east to west following the leaching events. This is indicated by maximum concentrations of 18 mg/L at well -18BCC1, and of 8 to 10 mg/L for -18BCC4, -18CBBC and -18BCCCB between 1996 and 2001, while maximum concentrations for three of four wells in the eastern portion of 134-057-13 were less than 4 mg/L. The lowest nitrate-N peak (< 2 mg/L) occurred in a well (13BDBB) located a quarter mile west of Englevale Road and the eastern boundary of Section 13. This may indicate that nitrate concentrations were highest in wells drawing water from the thin (eastern) portion of the aquifer overlying the divide. The thinner aquifer would have caused a larger relative proportion of contaminated water, and possibly greater nitrate retention because of more oxidizing conditions when influenced by well drawdown cycles. Conversely, in the deeper channel (farther west) a smaller proportion of shallow contaminated water would be withdrawn through the well screen.

Fig. 25 shows a cross section of the Englevale aquifer along the southern border of Section 134-058-25, with the inclusion of one well in Section 134-057-30. The elevated till divide discussed previously for the west half of 134-058-18 transverses the eastern half of Section 134-058-25 in the north-south direction. The aquifer forms a deeper channel toward the eastern boundary of the southwest quarter (-25D), which is

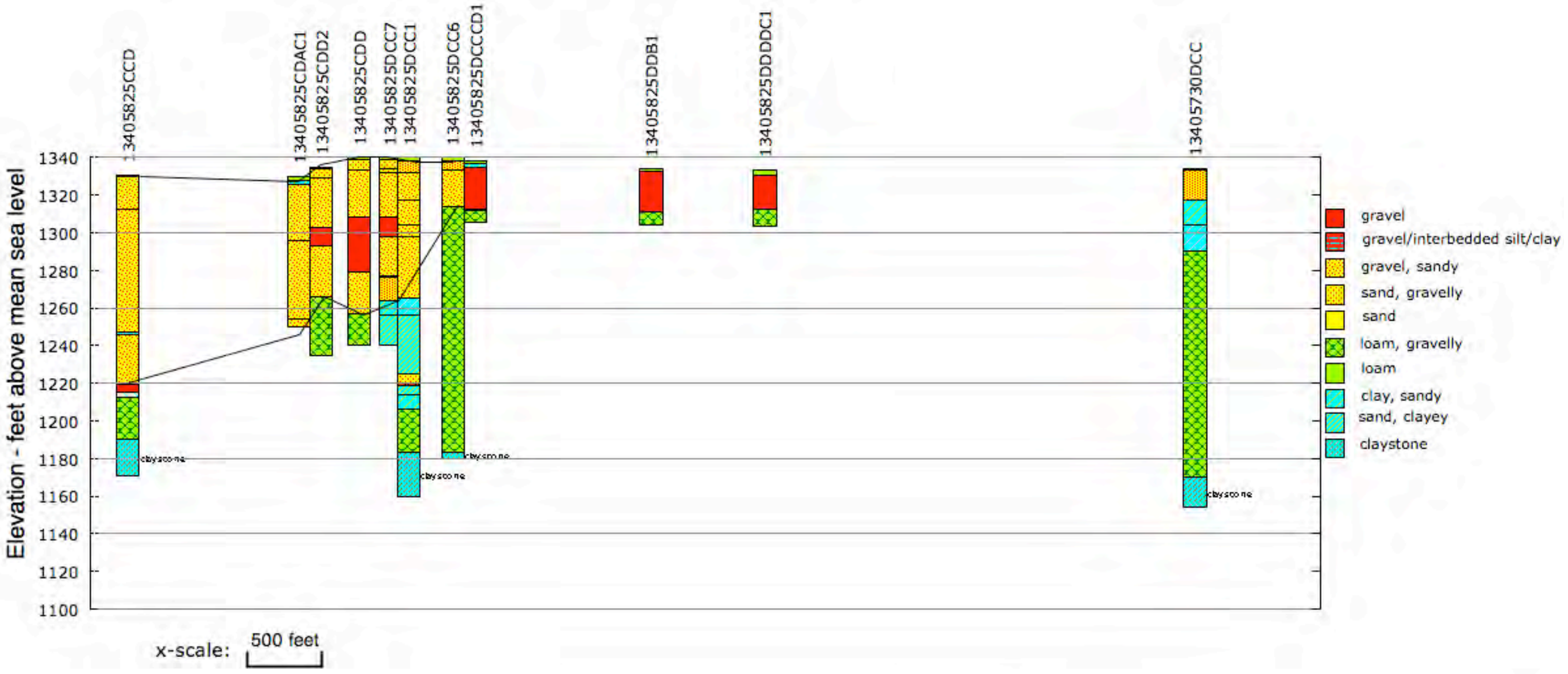

Figure 25. Stratigraphic transect for the middle Englevale aquifer (Township 134 N, Ranges 57 W and 58 W: USBLM 134-057 and 134-058)

sustained to the western boundary of the section (-25CDD). The temporal variation of nitrate-N concentrations, beginning in 1977, for an irrigation well (-25DCC) located in the southwest corner of the southeast quarter of Section 134-058-25, is shown on Fig. 26. Both the magnitude of changes and the trends are similar to irrigation well 134-058-13 AADD (Fig. 24), including a brief decrease in nitrate-N concentrations in 1997, a year having exceptionally large spring snowmelt.

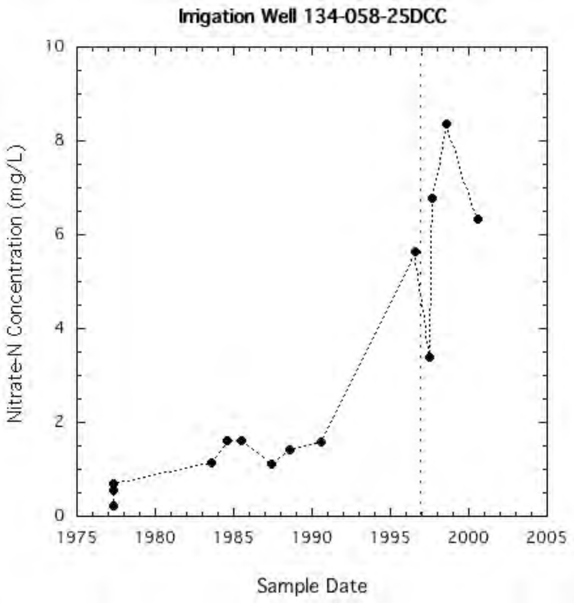

Fig. 26. Temporal variation of nitrate-N concentrations in irrigation well 134-058-25DCC.

Northeast Englevale Aquifer*: *Well Sites on 134-057-18, -19, and -30

Monitoring well sites in the northeast portion of the Englevale aquifer (134-057 USBLM) consist of seven sites in Section 18, one site in Section 19, and one site in Section 30 (Fig. 27).

Well sites *134-057-18DDD*, 134-057-19DCC and 134-057-30DCC are located east of and near a north-south till barrier that locally divides the east and west portions of the Englevale aquifer near the town of Englevale. The bottom of the aquifer is thus relatively shallow (about 20 feet bls). Aquifer flow is predominantly southward and slightly skewed westward (Fig. 2). The depth to the water table is periodically shallow (approx. 3 to 8 feet for -19DCC and 4 to 11 feet for -30DCC), and the saturated zone is relatively thin (approx. 12 to 17 feet for -19DCC and 9 to 16 feet for -30DCC).

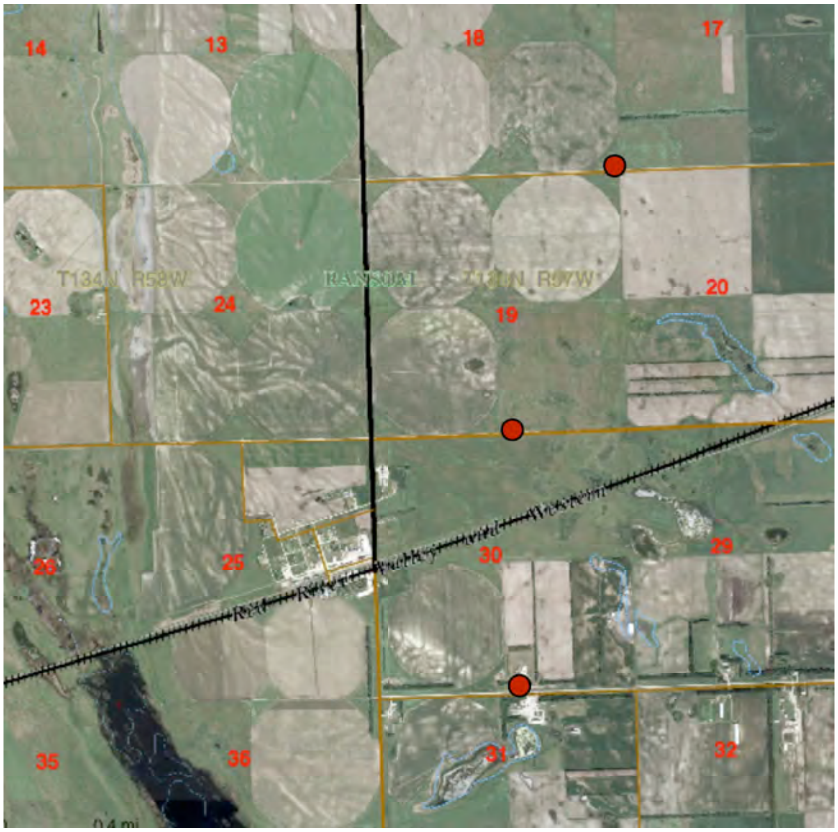

Figure 27. Location of monitoring well sites on Sections 134-057-19DCC and 134-057-30DCC.

All three sites are mapped to the Sioux-Renshaw soil series. The shallower water table on well site -18DDD, although mapped to the Renshaw-Sioux mapping unit, may indicate a transitional soil with more evapotranspiration. High water tables on this site may be partially affected by head buildup as the hydrologic system adjusts to north-south oriented till barrier. Soils are all classified as of Hapludoll Great Group taxa and function as predominant seasonal net recharge areas (Seelig and Richardson 1994). The shallow water tables would indicate that evaporation might be expected in some cases. However, low TDS in shallow wells on both sites would indicate that overlying soils likely have little salt concentration in them. The coarseness of the overlying soil likely limits evaporation through minimizing capillarity, and enhances flushing of salts from the local hydrologic system. Both well sites are located near the corners of irrigation systems, but are up-gradient from the irrigated tracts themselves. Both sites are down-gradient of non-irrigated tracts.

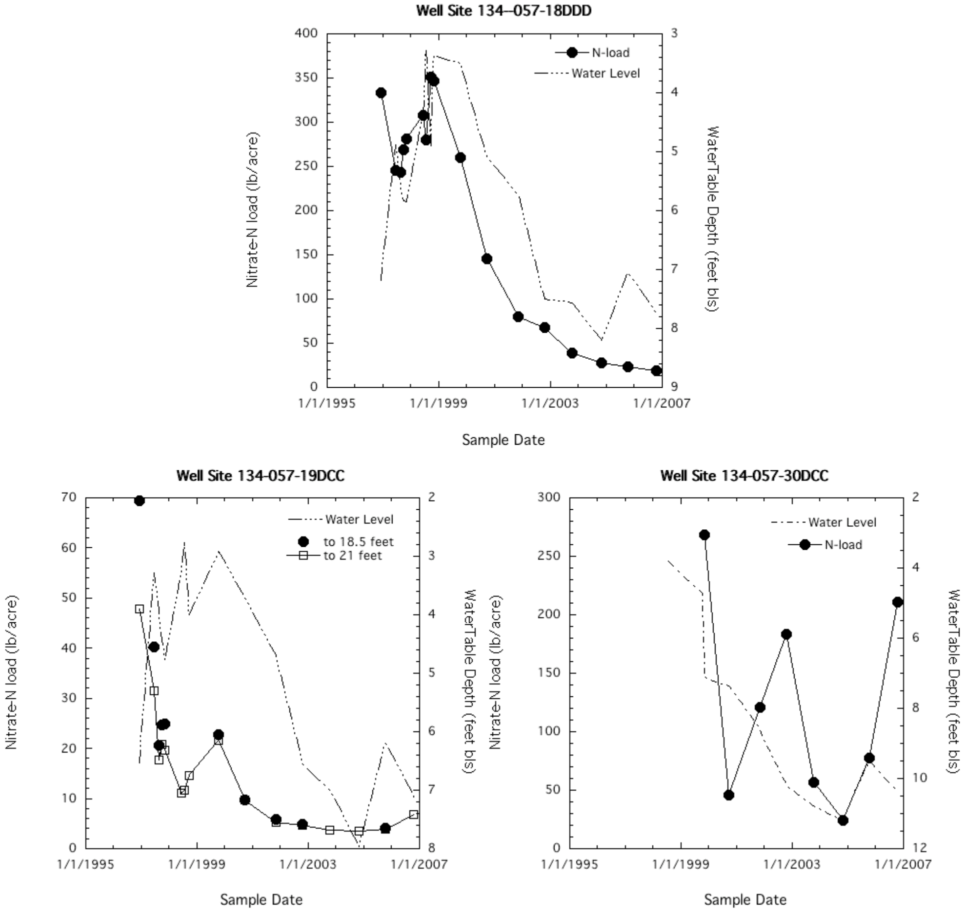

Figure 28. Nitrate-N load trends for Sections 134-057-18DDD, -19DCC and -30DCC well nests.

Nitrate-N Loading at Well Sites 134-057-18DDC, 134-057-19DCC and 134-057-30DCC

Initial nitrate-N loads at well site -18DDD were moderate to moderately high, but declined to low levels by 2002, and appear to have approximately stabilized in that range (Fig. 28). Well site -18DDD had a shallow depth to the water table. The less intense agricultural status of this location, and the shallower water table, which would tend to enhance denitrification through proximity to organic carbon in the upper soil horizons, both favor sustained low nitrate loading. Nitrate-N loads on site -19DCC were initially low, and progressed consistently to lower, and finally negligible levels at the end of the measurement period. Low nitrate-N may be partially due to up-gradient land use as non-tilled grassland. Site -30DCC was moderately high initially, with a maximum of about 200 lb./ac. equivalent load, and fluctuated between low and moderately high levels. Early total loads for -30DCC were not determined before 1999 because of excessive water-table elevation above the well-screen for reasonable load determination.

PMCI at Well Sites 134-057-18DDD, -19DCC and -30DCC

PMCI for -18DDC were initially high following leaching events in the mid 1990s, but declined steadily to very low concentrations by 2001 (Fig. 29). All PMCI for -19DCC were very low (<0.5 EPA-MCL) for all measurements. Final PMCI was negligible. The median PMCI for -30DCC was 6 mg/L, but fluctuated widely between 0.24 and 20.2 mg/L. PMCI values are increased under moderately high loads by the local thinness of the aquifer.

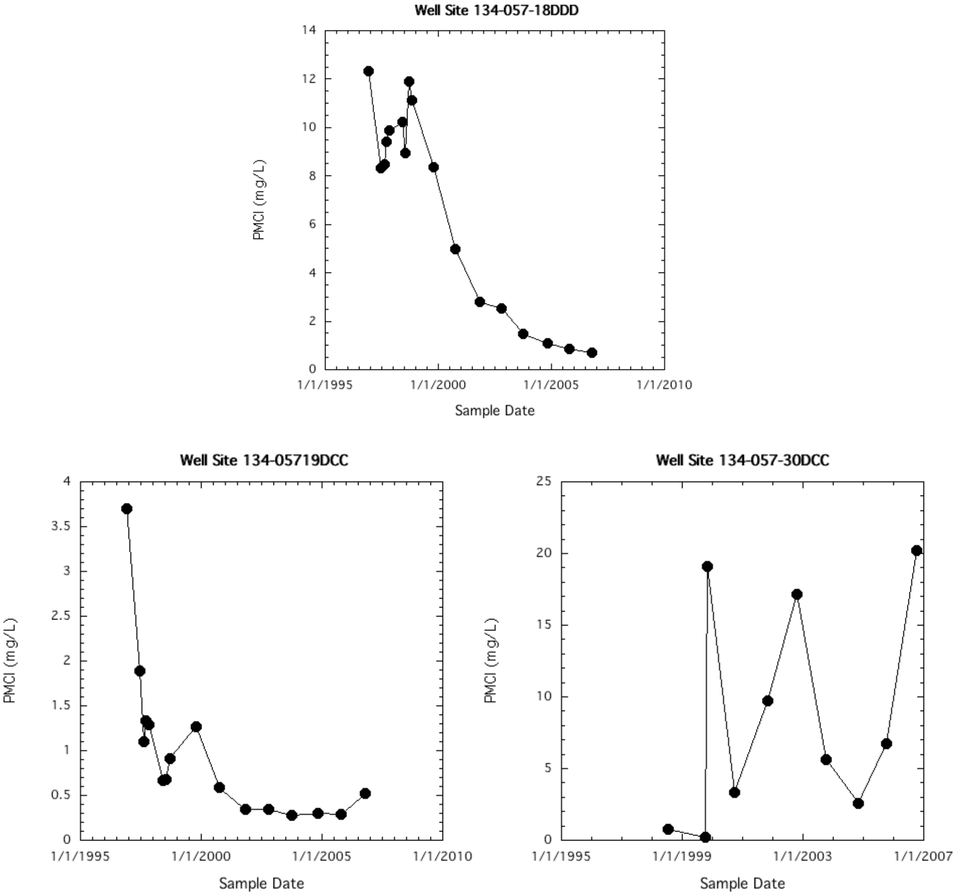

Figure 29. PMCI trends for Sections 134-057-18DDD, -19DCC and -30DCC well nests.

Causes of Nitrate Dissipation at Well Sites 134-057-18DDC, -19DCC and -30DCC

Dissolved oxygen at site -18DDC and -19DCC were initially high in the shallow wells, and moderately high in deeper wells, likely due to a thin saturated zone and aeration caused by recharge events. Eventually, however, DO decreased with the declining water table (Fig. 30). This indicates that there is likely a stable reducing zone wherein reducing minerals control the DO.

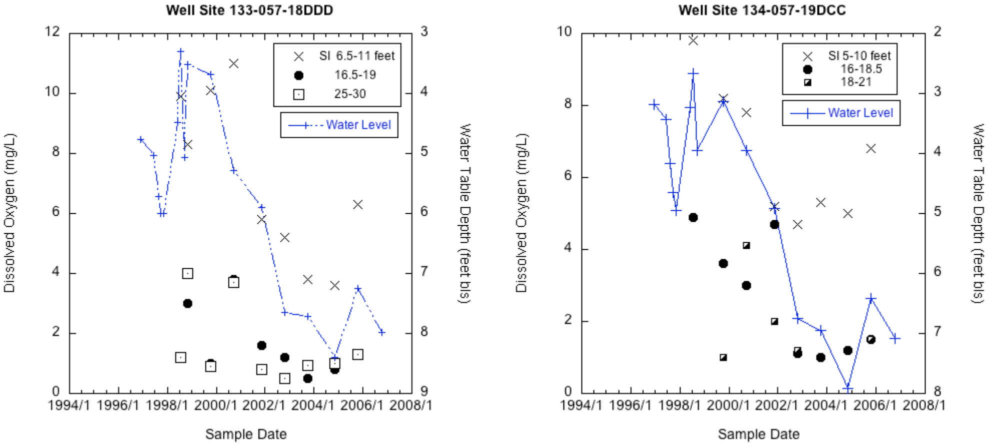

Figure 30. Dissolved Oxygen distribution with time and depth *bwt* for well sites 134-057-18DDD and 134-057-19DCC.

On site -19DCC there was a detectable inverse stratification of sulfate-S vs. nitrate-N within the deeper well-screen, indicating possible autotrophic denitrification occurring within the deeper well (Fig. 31). Site -18DDC exhibited no detectable inverse stratification of nitrate-N and sulfate-S. There is insufficient data to evaluate causes of nitrate loss on site -30DCC. We can speculate a contribution from denitrification based on water chemistry evidence and general indications of area denitrification from isotope data. Decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management.

Contamination Status at Well Sites 134-057-18DDD, -19DCC and -30DCC

Nitrate-N loads and PMCI at -18DDC were initially high, but declined to persistent very low values. Nitrate-N loads and PMCI at -19DCC were consistently low and are currently negligible. Nitrate-N loads and PMCI at -30DCC fluctuated from high to low. Thin saturated zones render PMCI sensitive to relatively small changes in nitrate-N loading. Median values on this site indicate that contamination is not of great concern. But additional caution in nitrate-management is warranted on neighboring fields due to fluctuating PMCI and sensitivity of toxicological indices to minor loading.

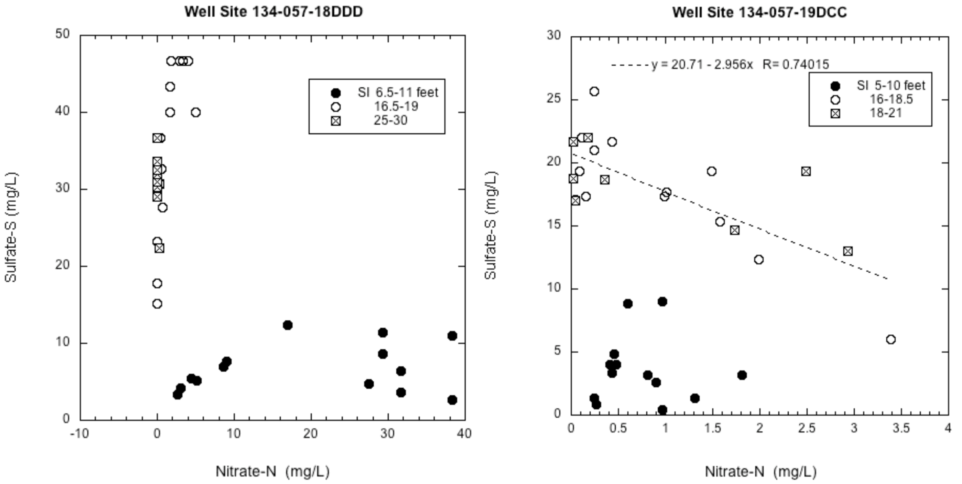

Figure 31. Sulfate-S vs. nitrate-N with depth *bwt* for well sites 134-057-18DDC and -19DCC.

Nitrate Summary at Well Sites 134-057-18DDD , -19DCC and -30DCC

Highest nitrate loads on both sites appear to have been caused by a leaching event preceding the measurement period (pre-1996). Nitrate-N loads vary between sites and over time. Generally they have decreased. Median PMCI indicate that none of the sites are in need of immediate remedial activity, although sensitivity to contamination due to thin saturated zones and fluctuations of PMCI 134-057-30DCC warrant additional caution in nitrate management.

West of the Till Divide: Well Sites on 134-057-18

Section 18 of Township 134 N and Range 057 W (134-057-18 USBLM) is located east of Englevale Road, about 1 ¼ mile north of Englevale. Agricultural use includes three irrigated tracts located in the NW, SW and SE quarter sections, and non-irrigated range land located in the NE quarter section. The flow system of Section 18 is divided by a till barrier transversing the western half-section in the north-south direction (Fig. 2). Water-table gradients east of the barrier are steep (approx. 0.005 in November of 1990) in the westward direction, possibly accumulating the head necessary to force water across the thin saturated thickness above the barrier, and tending on the south boundary of the section to bend southward. West of the barrier water-table gradients are predominantly north to south. Irrigation wells located along the western border draw water from both the deeper channel and from the shallower aquifer portion to the east (Fig. 22). Monitoring wells west of the till barrier are considered in this section.

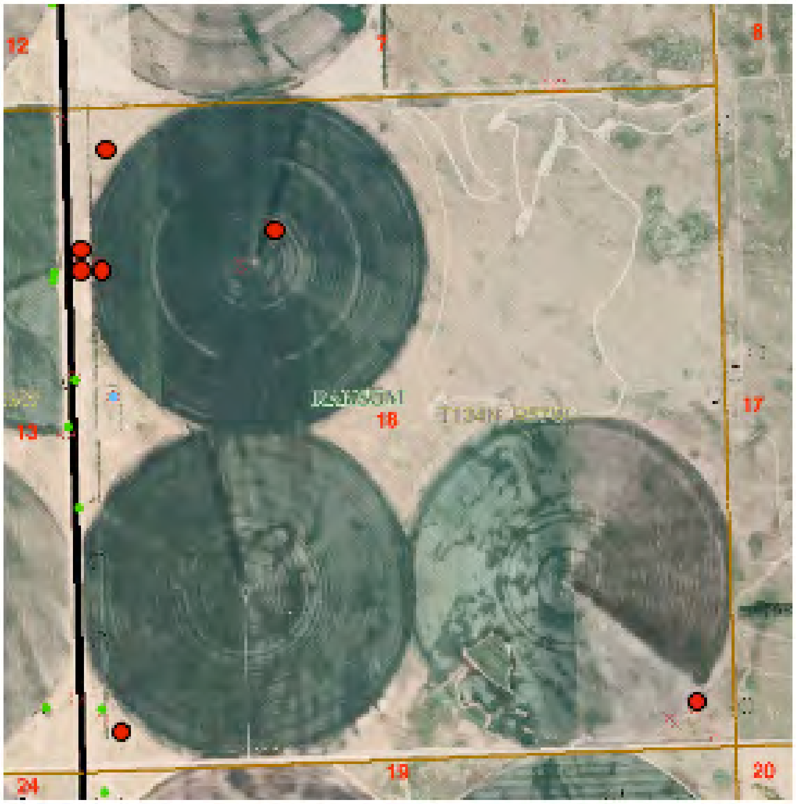

Figure 32. Location of monitoring well sites on Section 134-057-18.

Nitrate monitoring west of the till divide consisted of seven nested well sites (Fig. 32). These include: 134-057-18BAC, located near the center of the NW center pivot; -18BBB, located in the non irrigated NW corner of the NW pivot; -18BBCCC, located in the road ditch on the west border of the NW center-pivot near mid-field (where the irrigation trace is nearest the highway); -18BBCCD, located a few feet east of -18BBCCC west of the windbreak on the edge of the irrigated field; -18BCC, located in the SW non-irrigated corner of the NW quarter section; and -18CCC, located in the non-irrigated SW corner of the SW quarter.

Saturated thicknesses of the well sites (Table 1) are moderately thin, varying temporally from about 10 to 17 feet near the center of NW Section 18 (near the barrier), and temporal and spatial ranges of about 20 to 30 feet on the eastern and western borders of the section. Water tables are usually deep enough (11 to 20 feet) to cause uncoupled conditions with respect to ET. Corresponding soil series for all sites are Hapludolls of the Sioux-Renshaw, or Renshaw-Sioux mapping units, and may be considered as predominantly uncoupled seasonal recharge areas (Seelig and Richardson 1994).

Nitrate-N Loads in 134-057-18

Nitrate-N loads vary widely (Fig. 33). On two of the sites (-18BAC, and -18BBB) initial loads were moderate to moderately high, but declined to low (-18BAC) or very low (-18BBB) levels by 2002, and appear to have approximately stabilized in that range. Well site -18BAC has a thin saturated interval and is located near the center of a center pivot. All other sites have maintained moderately-high to high loads, ranging from about 200-to 600-lb./ac. equivalents.

General observations concerning nitrate-N loads are:

- Four of the six sites had their highest nitrate-N loads at the beginning of the measurement period in fall of 1996.

- Five of the six sites improved substantially (at least 50% reduction in estimated load) over the ten-year measurement period.

- Early high nitrate-N loads preceded rising water levels measured after 1997. This indicates that the peak loading events likely preceded the period of measurement, possibly initiated by large precipitation during and following 1993.

- During the period of measurement, increases in nitrate-N load generally corresponded with recharge events, as indicated by rising water tables.

PMCI in West Half of 134-057-18

Early PMCI values were above the EPA-MCL on all of the monitoring well sites (Fig. 34). At the end of the monitoring period, PMCI were very low (< 3 mg/L nitrate-N) on one site (-18BBB), moderately high (5 to 10 mg/L) on two others (-18BAC and -18BBCCC), and variable between high and moderately high (fluctuating near 10 mg/L) on two wells (-18BCC and -18CCC). One well (-18BBCCD) maintained sustained high values (between 15 and 30 mg/L).

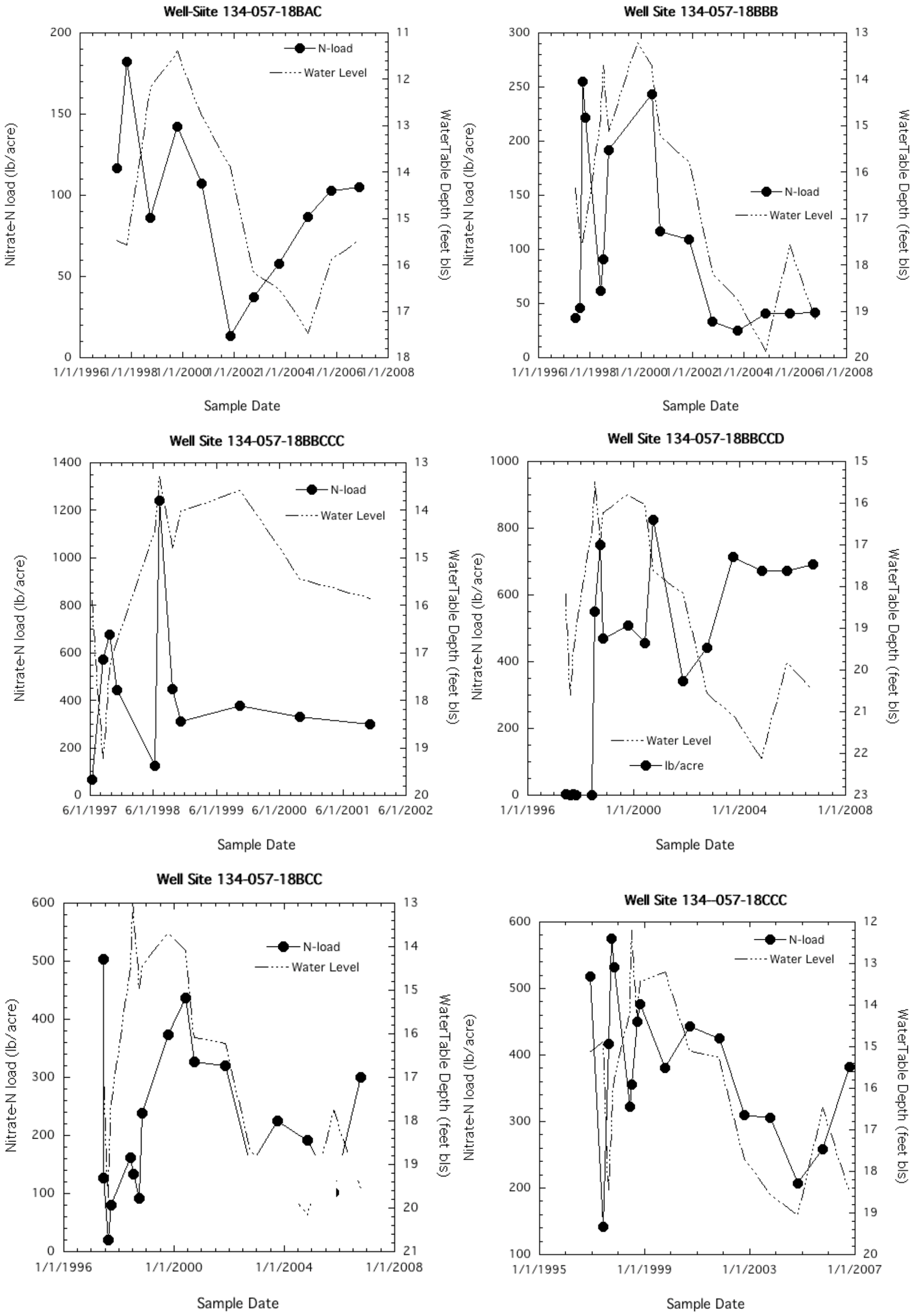

Figure 33. Nitrate-N load trends for well nests in the west half of Section 134-057-18.

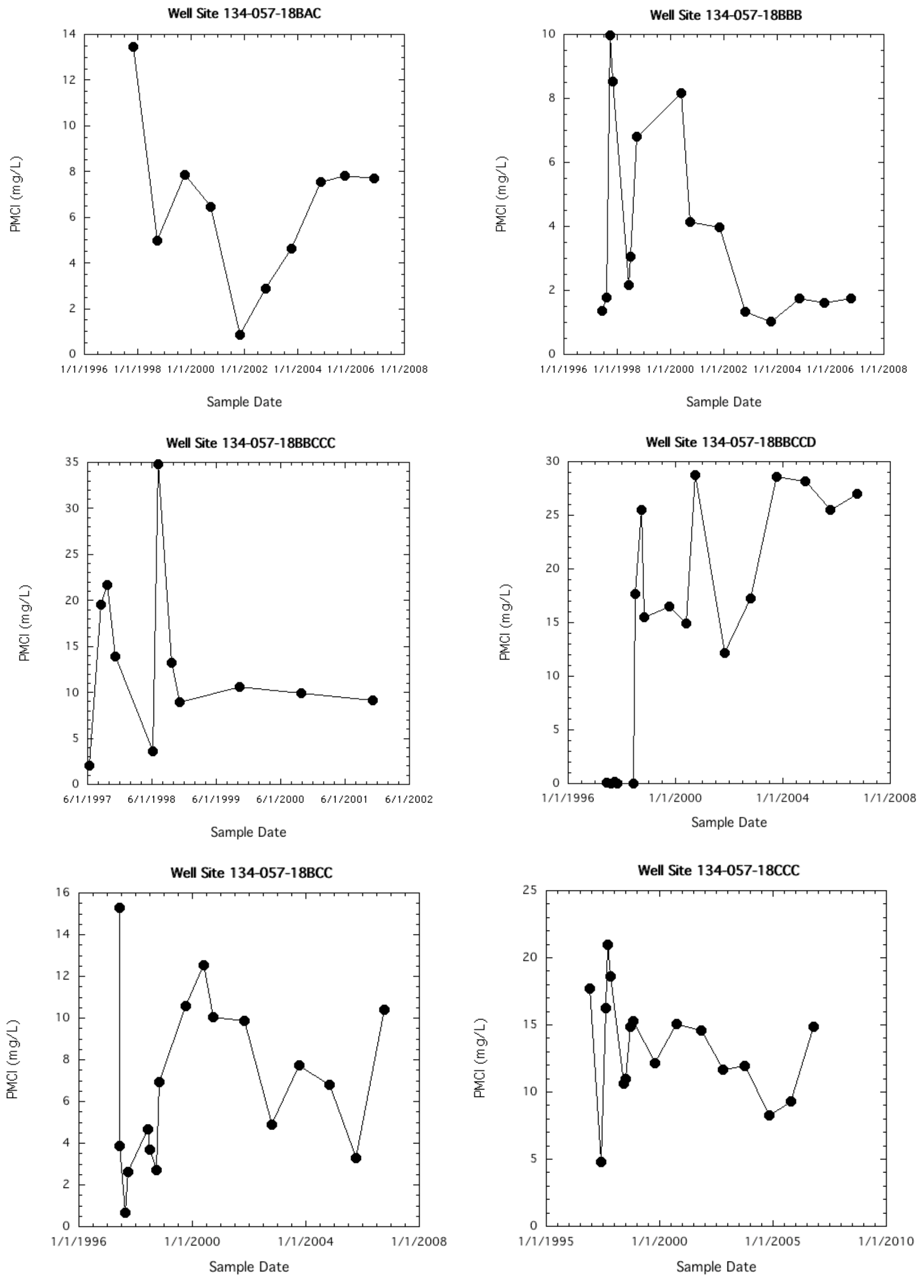

Figure 34. PMCI trend for Section 134-057-18 well nests.

Vertical Stratification of Nitrate Loading in 134-057-18

Nitrate concentrations in shallow wells were highly variable. While all well sites exhibited large decreases in total nitrate-N loads and PMCI, only four of the seven well sites exhibited sustained reduced final nitrate concentrations in shallow wells (Fig. 35). Three sites (-18BBCCC, -18BBCCD, and -18CCC) continued to exhibit nitrate replenishment in the upper aquifer.

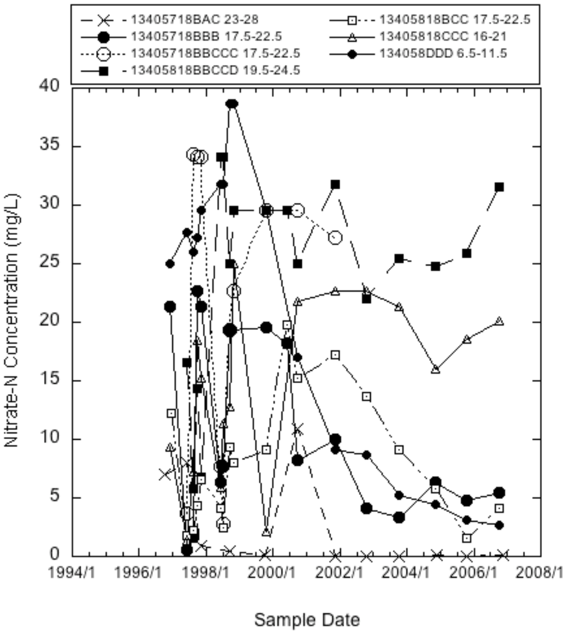

Figure 35. Nitrate-N trends in shallow wells on 134-057-18.

The trends of decreased nitrate-N loads with sustained shallow replenishment are explained by selective depletion of deeper nitrates over the monitoring period, as shown for -18BBB and -18CCC (Fig. 36). Concentration profiles on well site -18BBB exhibit both dissipation of nitrate-N in the lower profile and attenuated loading near the surface, while well site -18CCC exhibits dissipation in the lower profile with continued surficial loading. The trend of sustained surface loading combined with sustained dissipation of deeper nitrate support the previous observations that large initial loads were caused by events prior to 1996 (likely the wet climatic shift experienced during and following 1993), and that systemic natural remediation has been occurring since that time. Apparent stabilization of loads indicates that deep dissipation is nearly complete, and that current loads vary primarily with concentrations in the upper aquifer and patterns of characteristic leaching.

Causes of Nitrate Dissipation in 134-057-18

Of the six sites monitored, only -18DDD had a water table periodically shallow enough to allow for root-zone assimilation of nitrate from a ground-water source. All others were sufficiently deep to be essentially uncoupled. The consistency of dissipation at all sites indicates that denitrification or non-assimilative reduction is likely a significant contributor. Decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management following 1996.

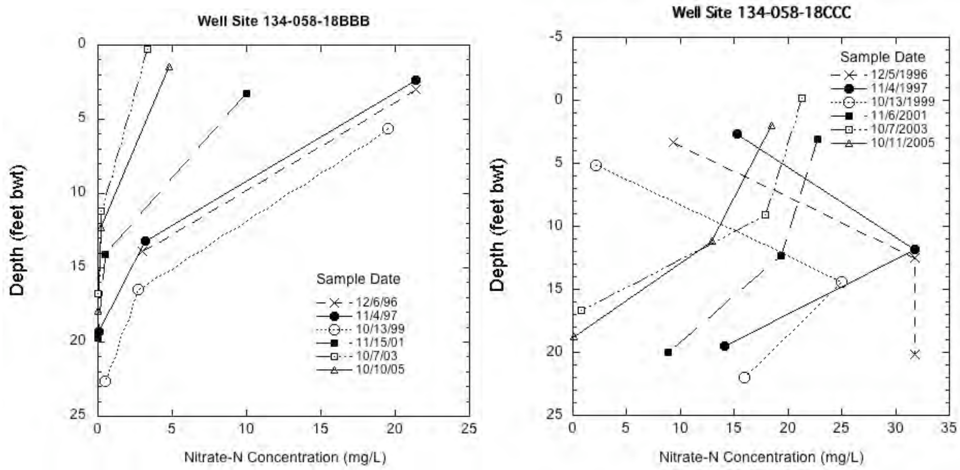

Figure 36. Vertical distribution of nitrate-N concentrations on well sites 134-057-18BBB (left) and -18CCC (right).

Isotopic analysis Isotopic analysis (^{15}N and ^{18}O) has indicated that denitrification is occurring generally in the Englevale aquifer. Water samples for two of the Section 134-057-18 well sites (-18BBCCC and -18BBCCD) were found to have elevated ^{15}N, indicating likely denitrification. Reducing conditions, indicated by low DO, are needed for denitrification. While DO varies temporally on all sites, all wells had DO predominantly below 2 mg/L within 15 to 20 feet below the water table (Fig. 37). Decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management.

Autotrophic denitrification using inorganic sulfide as an electron donor would be expected to cause increased sulfate concentrations in the deeper unoxidized portions of the aquifer where nitrate is dissipating. While sulfate concentrations are highly variable and no stoichiometric relationship can be discerned, inverse stratification in the sulfate-S vs. nitrate-N distribution with depth (Fig. 38) is clearly evident for well sites -18BBB, -18BBCCC, -18BBCCD, and -18BCC. On three sites, -18BBCCC, -18BCC, and

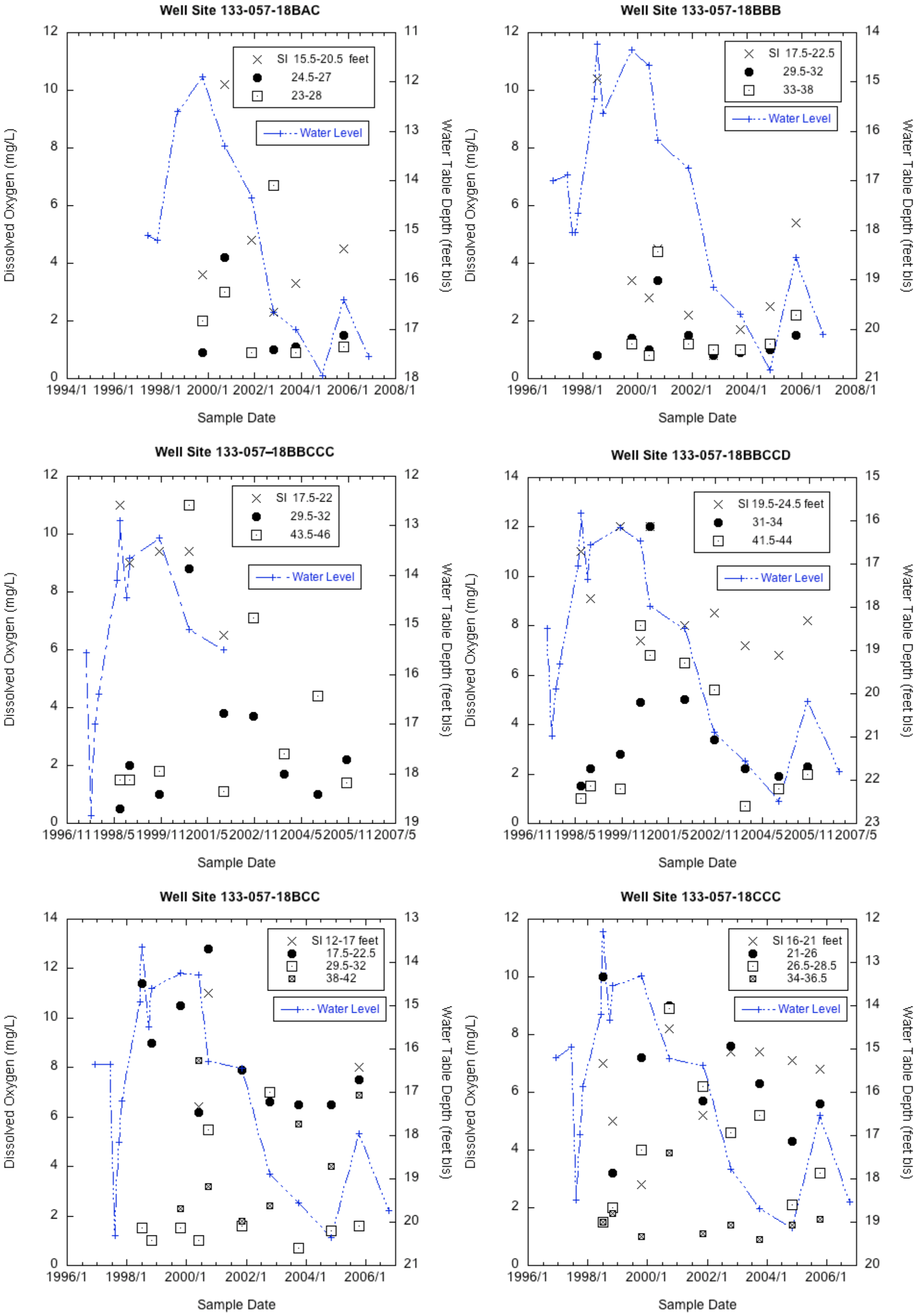

Figure 37. Dissolved Oxygen distribution with time and depth *bwt* for well sites in 134-057-18.

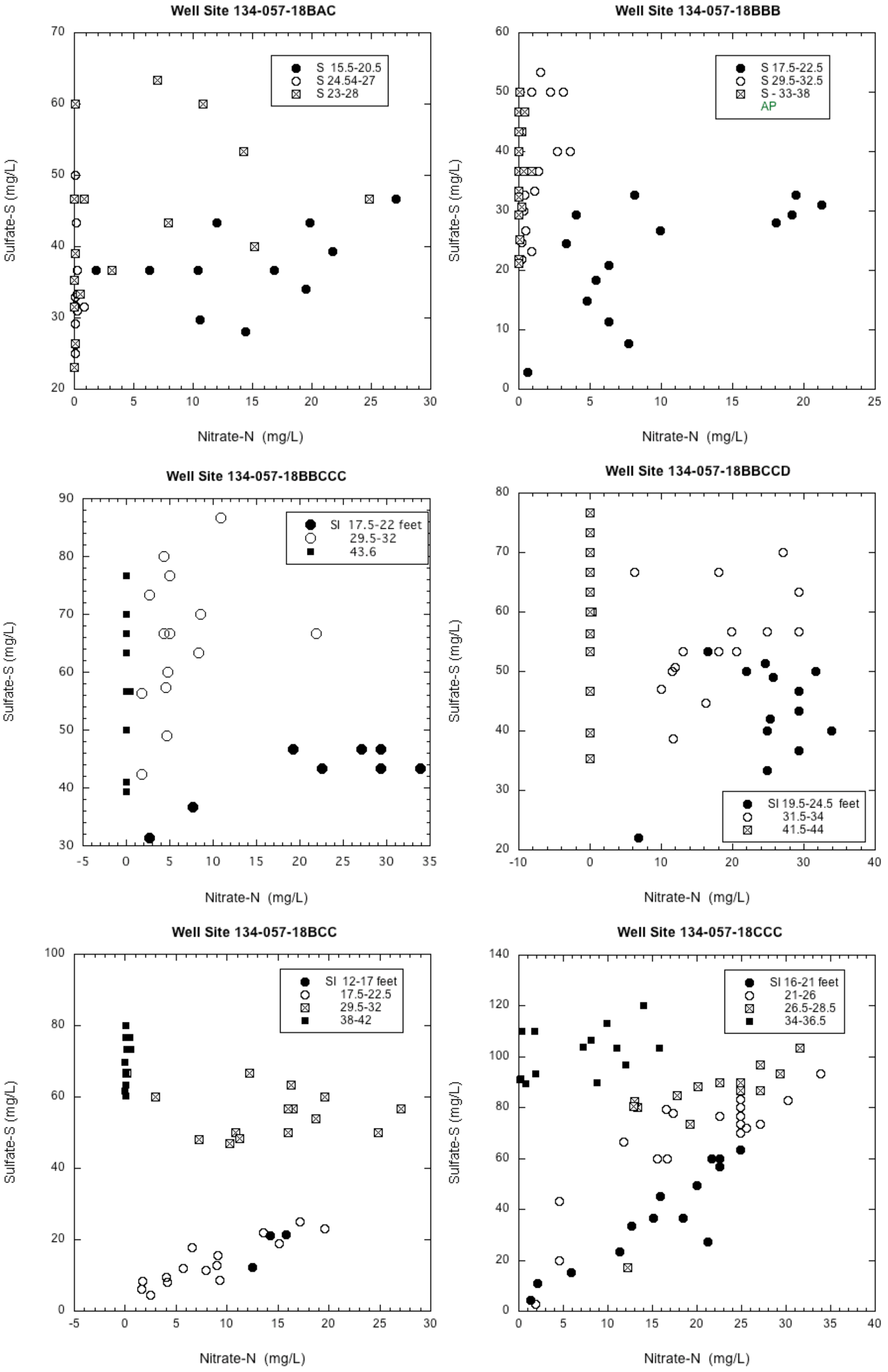

Figure 38. Sulfate-S vs. nitrate-N distribution with time and depth for well sites on 134-057-18.

by companion leaching of nitrate and sulfate from the vadose zone. Sources could be -18CCC a double pattern for sulfate-S vs. nitrate-N is evident. The increasing sulfate-S with decreasing nitrate-N pattern is evident between layers, but within the shallowest well samples, and within the shallowest two wells for well site -18BCC, a strongly correlated positive linear relationship for sulfate vs. nitrate is evident. This would likely be caused 7ulfate-containing fertilizer, such as ammonium sulfate.

Alternately, it has been shown that sulfate and other soluble anions tend to accumulate under dryland conditions just beneath the root zone at a depth of about seven feet (Schuh and others 1997). A large rainfall may have flushed both nitrate and sulfate from the zone of accumulation on these sites.

The close correspondence of declining nitrate-N loads and water-table depths may be caused by the constriction of the oxidized layer between the water-table surface and the denitrifying zone and the subsequent forcing of denitrification of stored nitrate. Several authors, including Kolle and others (1985) and Böhlke and others (2002) have observed that the depth of the unoxidized zone is determined by the presence of reducing minerals, and that the progressive depletion through oxidation of those minerals causes a slowly advancing front and deepening of the oxidized zone. A similar observation has been made of the Elk Valley aquifer in eastern North Dakota by Dr. Simon Bottrell, (Schuh, Bottrell and Korom 2006), where the oxidized zone is characterized by an upper strata depleted of pyrite-S and the reduced zone has retained large reserves of pyrite.

While we have no mineral data for the Englevale aquifer, DO data indicate that, except for small pulses of ephemeral DO during recharge events, DO in deeper wells is not significantly affected by the declining water table. In such a case, the retention of nitrate will be enhanced by a thicker oxidized zone and consequent reservoir of nitrate more distant from the reducing minerals. Aquifer depletion would force nitrate in the overlying oxidized reservoir into the proximity of mineral electron donors. Nitrate in the thinner oxidized zone would then be depleted. In this case, in the presence of a chemical reducing layer, the fluctuation of the water table in and of itself may provide an important mechanism in controlling denitrification.

Contamination Status of Individual Well Sites in 134-058-18

- Well site 134-057-18BAC has low PMCI. The current nitrate status is acceptable and should be maintained.

- Well site 134-057-18BBB has very low PMCI. The current nitrate status is acceptable and should be maintained.

- Well site 134-057-18BBCCC has a high (approx. 10 mg/L) PMCI. Slight improvement through decreased loading is desirable.

- Well site 134-057-18BBCCD has a high nitrate-N load and a PMCI consistently greater than 2x the EPA-MCL. Significant improvement through decreased loading is desirable.

- Well site 134-057-18BCC has a marginally high (approx. 10 mg/L) PMCI. Slight improvement through decreased loading is desirable.

- Well site 134-057-18CCC has a marginally high (approx. 10 mg/L) PMCI. Slight improvement through decreased loading is desirable.

Nitrate Summary for 134-057-18

Aquifer nitrate-N loads in Section 134-057-18 vary widely within relatively short distances. There is no clear evidence of accumulation or dissipation along the flow path toward Englevale Slough. More likely - nitrate concentrations reflect local events, with some possible displacement and dispersion. A pattern of initial high nitrate-N concentrations and loads, and initially deeper penetration of N followed by later dissipation, indicates that large nitrate-N influx likely occurred before the period of measurement, possibly in the very wet years beginning in and following 1993. Previous discussion of climatic variables indicates that nitrate-N loads are strongly affected by climate. Decreasing nitrate concentrations are likely caused by denitrification in the deeper aquifer. This is further supported by evidence of decreasing nitrate in deeper wells, while concentrations in shallower wells are sustained. Isotopic evidence, DO distributions, and inverse (and sometimes highly correlated) stratification of nitrate and sulfate with depth all support the theory that denitrification is a significant cause of dissipation. Improvement has been substantial. Approximate stabilization of nitrate-N loads and PMCI indicate that final dissipation rates are being approximately equaled by ongoing replenishment. PMCI indices of toxicological impairment are affected by both nitrate loads and local saturated thickness. They indicate that four of seven sites are in good condition, and three more are marginal with respect to accepted toxicological standards. One is high. Despite significant progress, further improvement, through decreased nitrate loading, is desirable.

Northwest Englevale Aquifer (Township 134 N, Range 58 W)

Monitoring well sites in the northwest portion of the Englevale aquifer (134-058) consist of one site each in Sections 1,10,12,13, and 14 (Fig. 39) and six sites in Section 25 (Fig. 44).

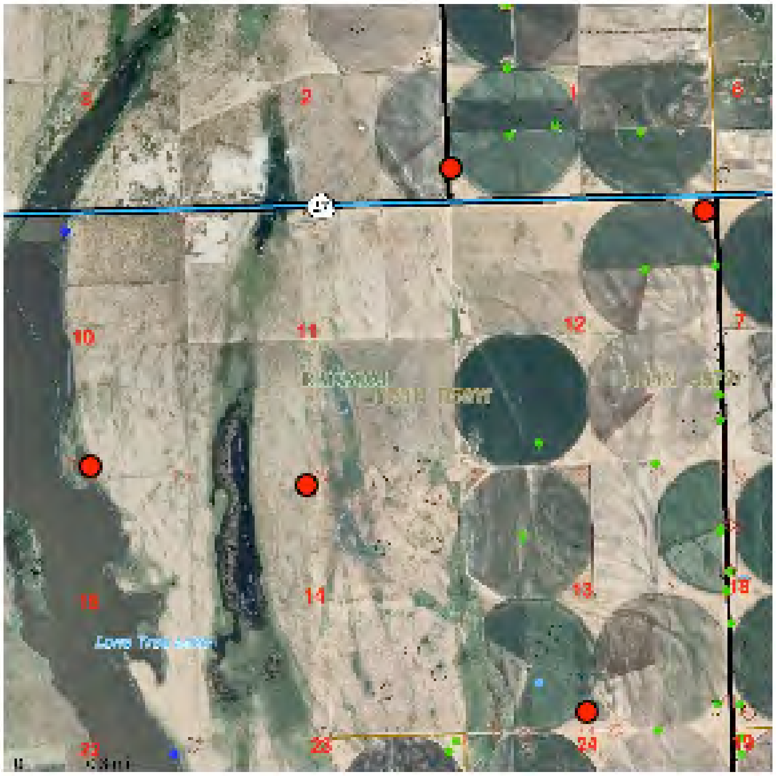

Figure 39. Location of monitoring well sites on 134-058, Sections -01, -10, -12, -13, and -14.

Wells Sites on 134-058-01, -10, -12, -13 and -14, Northwest Englevale Aquifer

There are five widely-distributed well nests in the northwest area of the Englevale aquifer between State Highway 23 on the north, the town of Englevale on the south, Lone Tree Lake on the west, and Englevale Road on the east. Well site -01CCB is just north (within a few hundred feet) of the north boundary on Highway 23. It is located in the corner of an irrigated quarter section, and down-gradient of three irrigated quarter sections. Site -12AAA is located in a corner bordered by three irrigated quarter sections (generally down-gradient). Site -13CDD is bordered by irrigated quarter sections on four sides. Site -14BAA is located in grassland fields at least ¼ miles down-gradient of the nearest irrigated field, and is located near the wetland complex associated with Lone Tree Lake. Site -10DCC is located near Lone Tree Lake, which, with its associated wetlands, comprises the natural local destination and sink for the Englevale aquifer.

All wells are located in net recharge areas within an aquifer flow system that is southwestward toward Lone Tree Lake, and the associated wetland complex near the lake. The grain matrix is generally coarse sand, gravel and pebbles. Detrital shale is present in some layers. Saturated thicknesses vary from negligible (-01CCB) at the northern limit to as much as 125 feet (-13CDD) at the southern limit. Water-table depths are generally deep enough to be uncoupled with respect to ET. Soils are all mapped as Sioux-Renshaw, or Renshaw-Sioux. Site -10DCC is located at the top of a break in slope that drops down into a low area which extends to Lone Tree Lake. Soils in the low area are mapped as the Southam series. Sioux and Renshaw soils are Hapludolls, and therefore net recharge areas, which is consistent with measured water-table depth ranges on all sites.

Nitrate-N Loading at Well Sites 134-058-01CCB , -10DCC, -12AAA, -13CDD, -14BAA, Northwest Englevale Aquifer

All nitrate-N loads on all sites are less than 300 lb./ac. at all times, and low (< 100 lb./ac.) on four of five sites by the fall of 2006 (Fig. 40). Three of the well sites (-10DCC, -13CDD, and -14BAA) had their highest values at earliest measurement times, indicating that nitrate contamination occurred in an event before the period of measurement, possibly the wet climatic period between 1993 and 1997. All three declined to less than 1/3 of their initial loads.

PMCI Indices in the Northwest Englevale Aquifer, at Well Sites 134-058-01CCB, -10DCC, -12AAA, -13CDD, and -14BAA

Except for three PMCI measurements (Fall 2002, 2003 and 2005) on site -01CCB which were slightly above 10 mg/L, all PMCI were low to very low (< 3 mg/L) (Fig. 41). Final (2006) PMCI for four of the sites were very low, and one was slightly (approx. 4 mg/L) above the very low category. Values and trends for PMCI indicate that all of these sites are in good condition with respect to nitrate contamination.

The causes of temporary elevated nitrate differed considerably between well sites. Sites -10DCC and -14BAA are both located in the grassland and slough complex west of the irrigated area and had low (10-to 12-ft.) saturated thicknesses. Relatively low PMCI were caused by low nitrate-N loads. Conversely, Sites -12AAA and -13CDD have large saturated thicknessses (approx. 55 and 120 ft., respectively). Relatively low PMCI are caused by thickness of the aquifer rather than low loading rates. Site -01CCB had a persistently high PMCI because of its location within an irrigated area, and a moderatly high load, combined with a low (approx. 10 ft.) saturated thickness.

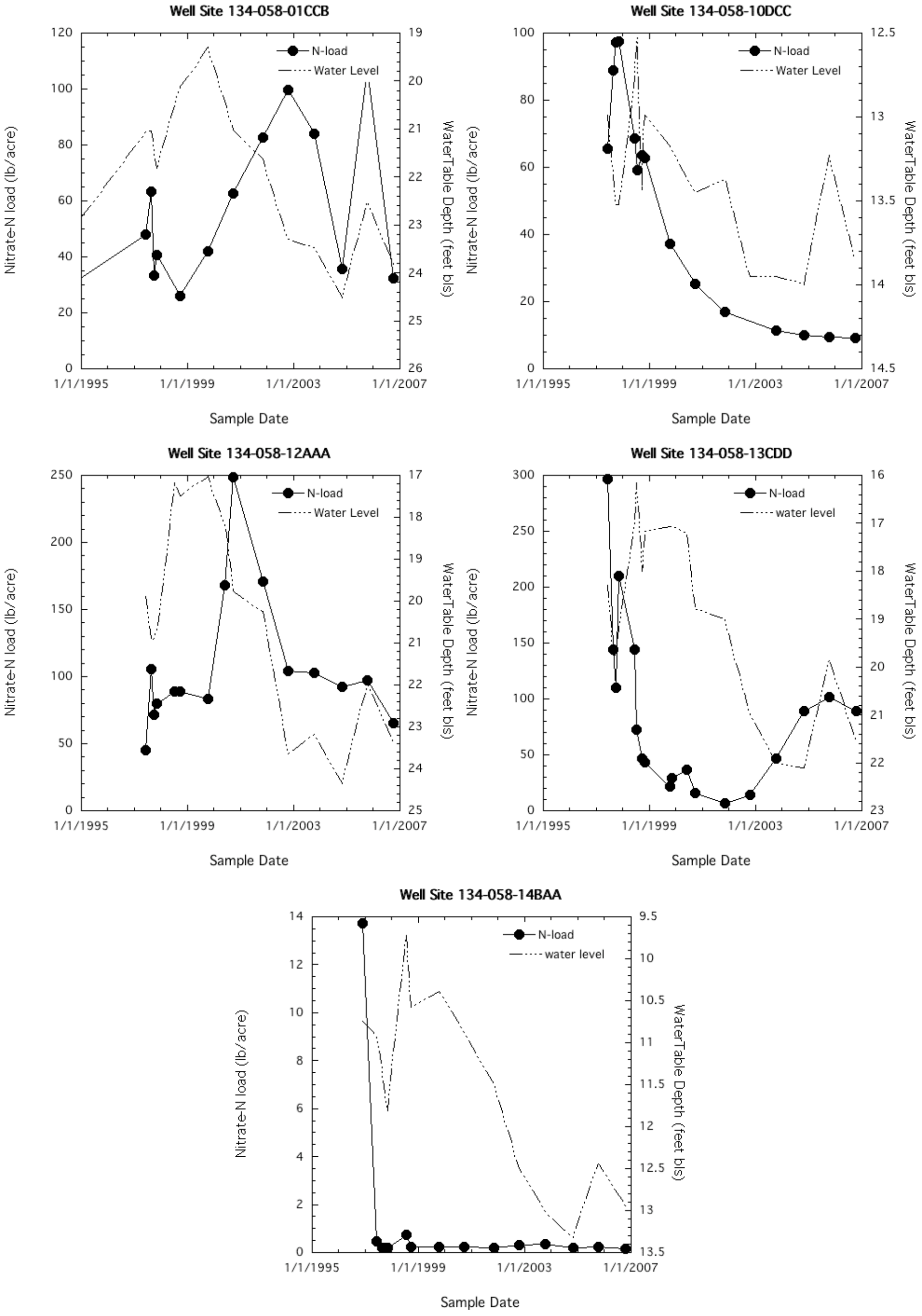

Figure 40. Nitrate-N load trends for 134-058, well sites -01CCB , -10DCC, -12AAA, -13CDD, and -14BAA

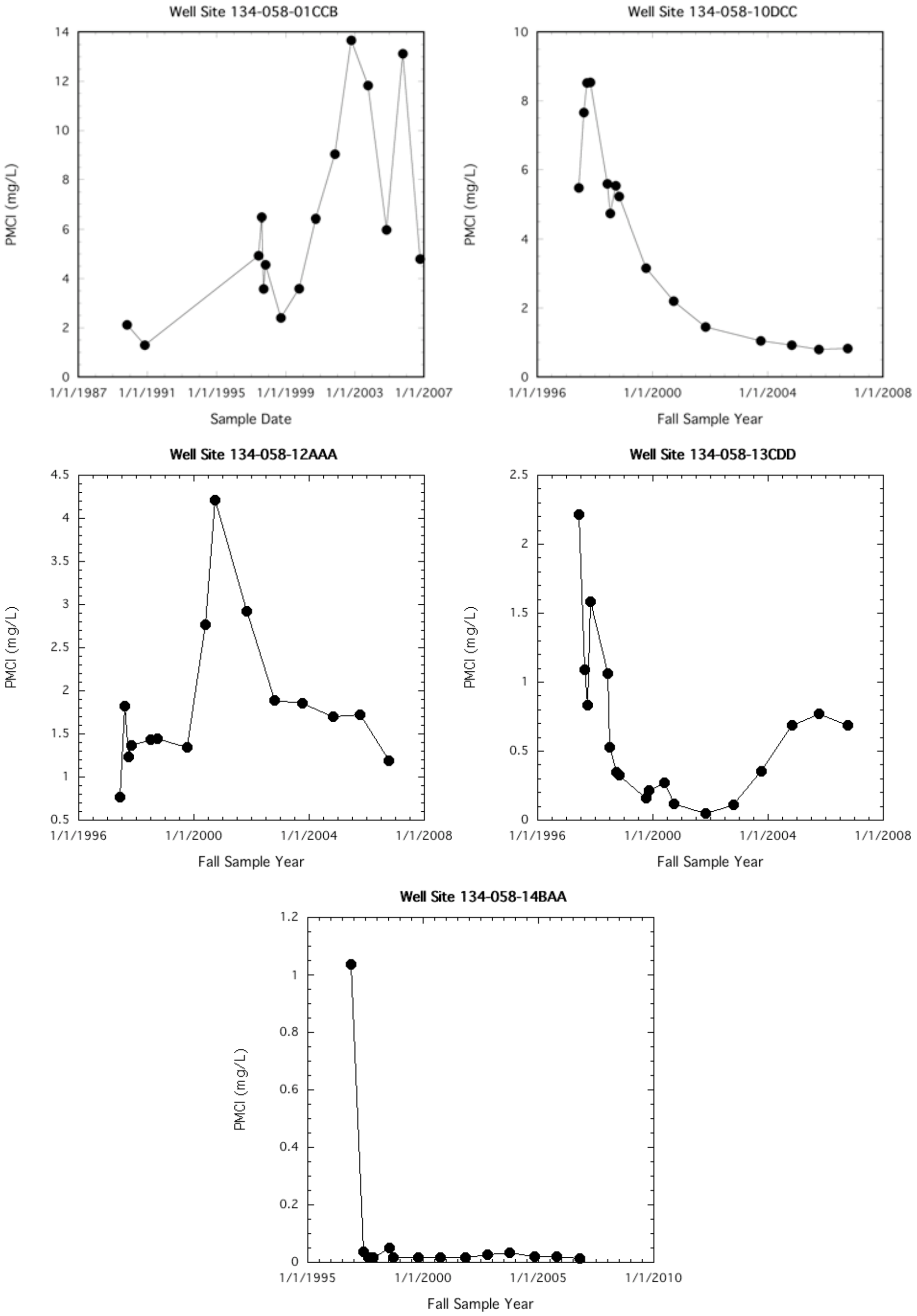

Figure 41. PMCI trends for Section 134-058, well sites -01CCB , -10DCC, -12AAA, -13CDD, and -14BAA.

Causes of Nitrate Dissipation at Well Sites 134-058-01CCB, -10DCC, -12AAA, -13CDD, and -14BAA

Dissolved oxygen for both -01CCB and -10DCC were relatively high (Fig. 42). Both sites had low saturated thickness so that recharge waters likely governed the oxidation-reduction states (Table 1). Similarly, sulfate-S vs. nitrate-N for both sites was positively correlated (Fig. 44), indicating that sulfate and nitrate were likely companion anions in leachate from the vadose zone and that sulfate generation from autotrophic denitrification was not indicated on either site. Both sites had low to very low nitrate-N loads. Intermittent denitrification periods or dispersion of localized contamination could account for nitrate dissipation on these thin (and highly sensitive) sites.

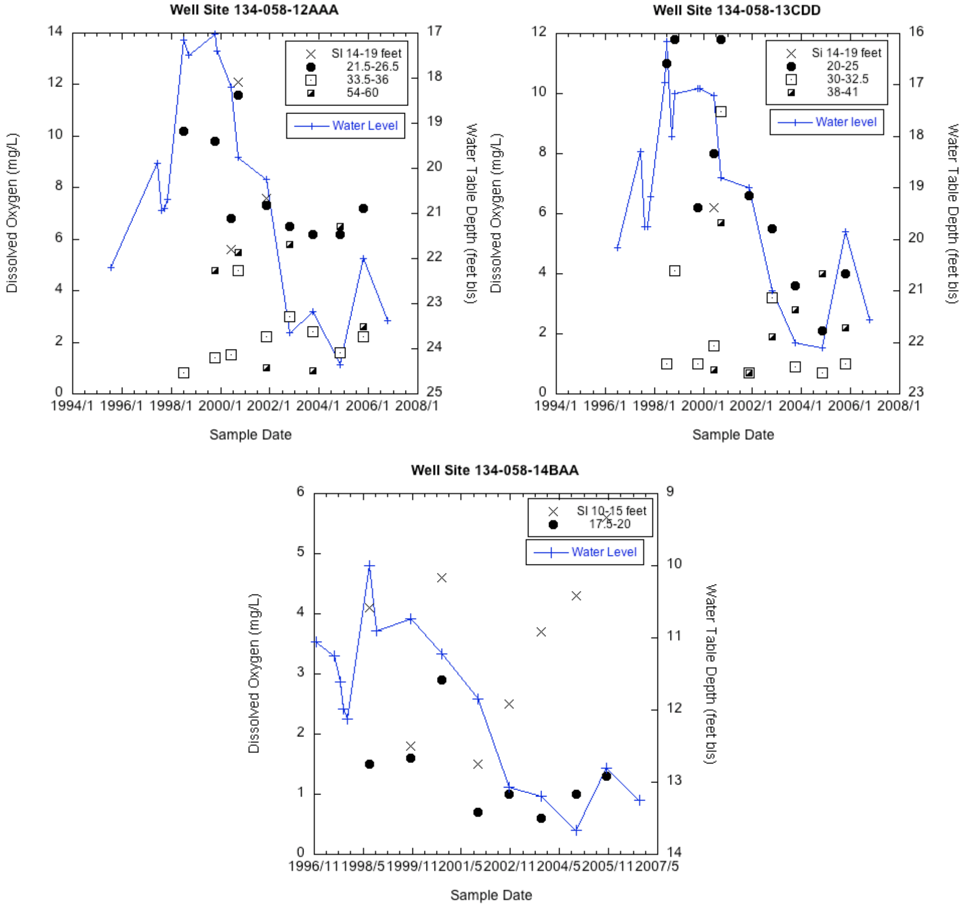

Figure 42. Dissolved Oxygen distribution with time and depth for 134-058, well sites 134-058-12AAA, -13CDD, -14BAA.

Well sites -12AAA, -13CDD and -14BAA initially exhibited low DO within 20 feet of the water table. Low DO was sustained at less than 10 feet below the water table as it declined (Fig. 42). Site -14BAA had low DO very near the water table. The sustained low DO in these layers, even as the water table declined, and in spite of periodic recharge events, indicates that they are controlled by reducing minerals within the grain matrix. The stable reducing layer and covariance of declining nitrate with a falling water table indicate that declining water tables may serve to draw nitrate into closer proximity with the stable reducing layer, enhancing local nitrate dissipation. Decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management following 1996.

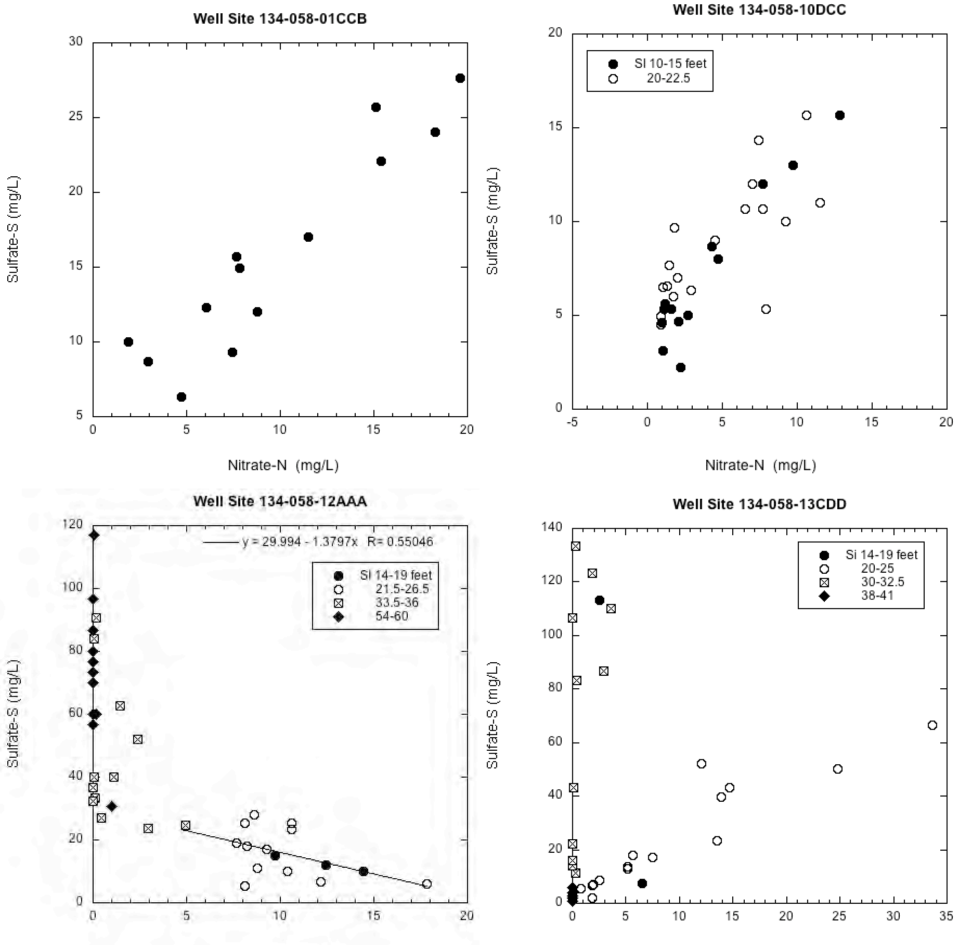

Figure 43. Sulfate-S vs. nitrate-N distribution with time and depth for 134-058, well sites 134-058-01CCB , -10DCC, -12AAA, and -13CDD.

Low DO indicates an environment conducive to autotrophic denitrification. Sulfate-S and nitrate-N were inversely stratified with increasing depth on both sites -12AAA and -13CDD (Fig. 43). The relationship for well site -12AAA is highly correlated in the upper two well-screen sample depths with a coefficient (1.39) close to the stoichiometric expectation (1.63) for autotrophic denitrification using combined pyrite sulfur and iron as electron donors. Sulfate-S vs. nitrate-N with depth on site -13CDD is complex, with a positive correlation within the shallowest well screen (indicating likely companion anion leaching from the vadose zone), but with a general inverse relationship with increasing depth, indicating possible autotrophic denitrification. The relationship for well site -14BAA (not shown) was random. Nitrate loads on this site were so consistently low, that neither substantial leaching nor denitrification would be expected to be evident.

Combined evidence indicates that conditions were usually non-conducive for denitrification on sites -01CCB and -10DCC, mainly due to a thin aquifer and subsequent dominance of aerated recharge waters in controlling and maintaining relatively high DO. Sites -12AAA and -13CDD displayed ambient conditions conducive to denitrification, and sulfate profiles consistent with autotrophic denitrification. Nitrate loads on site -14BAA were consistently too low to expect significant evidence of nitrate reduction. Nitrate concentrations were stratified, similar to other areas (not shown).

Contamination Status of Individual Well Sites in the Northwest Englevale Aquifer

All well sites are in good condition with respect to nitrate contamination. Because of thinness, -01CCB and -10DCC and -14BAA are highly sensitive to nitrate contamination. Sites -10DCC and -14BAA are both located within grasslands. Current management, however, seems to provide adequate protection at these locations. Changing agricultural use, however, could cause large changes in nitrate status on these sites. Normal caution is advised.

Nitrate Summary for the Northwest Englevale Aquifer

Nitrate levels and PMCI are consistently low in this portion of the aquifer, and have improved over the ten-year measurement period. Three of the sites likely have little denitrification because of thinness of the saturated zone and dominance of aerated surface recharge waters. Two have conditions conducive to denitrification, and exhibit chemical indicators that autotrophic denitrification may be occurring. These sites are generally in good condition with respect to nitrate concentrations.

Figure 44. Location of monitoring well sites on Section 134-058-25.

Location and Characteristics of Well Sites on 134-058-25

Section 25 of Township 134 N and Range 058 W (134-058-25 USBLM) extends from the town of Englevale (in the south half of the northeast quarter) to Englevale Slough on the western border. Agricultural land use includes slightly more than a half a quarter section of dryland crop land in the northeast quarter section, north of Englevale, an approximate half pivot (about 115 acres) in the northwest quarter section, an approximate 62-acre center pivot in the southwest quarter section, and an approximate 82-acre center pivot in the southeast quarter section. Variably cropped dryland fields also lie on the western borders of the section, between the center pivots and Englevale Slough.

Well sites 134-058-25DDDDC, -25DDB, -25DCCCD, -25DCCCC, -25CDAC, and -25CCD extend sequentially eastward along an approximate transect in the south half of Section 25 (Fig. 44). Area ground water flows predominantly from north to south (Fig. 2). Well sites -25DDB and -25CDAC are in the centers of the southeast and southwest pivots, respectively. The others extend along the southern border of the section. A cross sectional transect for the south border of Section 25 is shown on Fig. 25. The elevated till aquitard divide discussed previously for the west half of 134-058-18 transverses the eastern half of Section 25 in the north-south direction. The aquifer forms a deeper channel toward the eastern boundary of -25D which is sustained to the western boundary of the section (-25CCD, Fig. 25).

The average horizontal water-table gradient was estimated from maps for three dates (5/30/79, 11/11/85 and 11/25/90) at about 0.001. The upper aquifer was usually composed of predominantly coarse sands or gravel. Rough estimates based on composite horizontal K values of 300 to 500 feet-per-day and a transmitting porosity of about 0.3, would indicate a range of darcian flux values from 110 to 190 feet per year, and mean conservative solute movement rates of about 360 to 600 feet per year.

While depths to water vary from a minimum of about 8 feet on one site (-25CDAC, Table 1) to a maximum of about 19 feet on another (-25DCCCD, Table 1), all well sites have water tables that are sufficiently deep to be predominantly uncoupled. Root extraction of water (and solute) from water tables deeper than 8 feet have been described as minimal for sandy soils (Benz, Doering and Reichman 1981). All well sites underlie soils of the Hapludoll Great Group taxa (Table 1), which have been been described as hydrologically associated with seasonal recharge areas (Seelig and Richardson 1994) and as having minimal local ET. Decreases in nitrate concentrations are thus expected to occur through dilution and spreading, denitrification, or fixation as ammonium.

Nitrate-N Loads in 134-058-25

Nitrate-N loads vary both spatially and temporally, from negligible loading to local load equivalents as high as 1,850 lb./ac. A summary of nitrate-N loads for Section 134-058-25 is shown on Fig. 45. Several observations of general trends can be made. These are:

- Five of the six sites had their highest loads at the beginning of the measurement period in fall of 1996. The exception to this was -25DDDDC in the southeast corner of Section 25, which increased in load over time, but which at all times had very low nitrate loads.

- All of the well sites having large initial loads (five of six sites) decreased substantially over the ten-year measurement period, to between a third and a half of their initial loads.

- Although there is a minor correspondence between increasing nitrate-N loads and minor recharge events, particularly late in the measurement period, the earlier and apparently larger recharge events (represented by increasing water tables) lagged behind the initial high loading rates, and appeared to be associated with freshening.

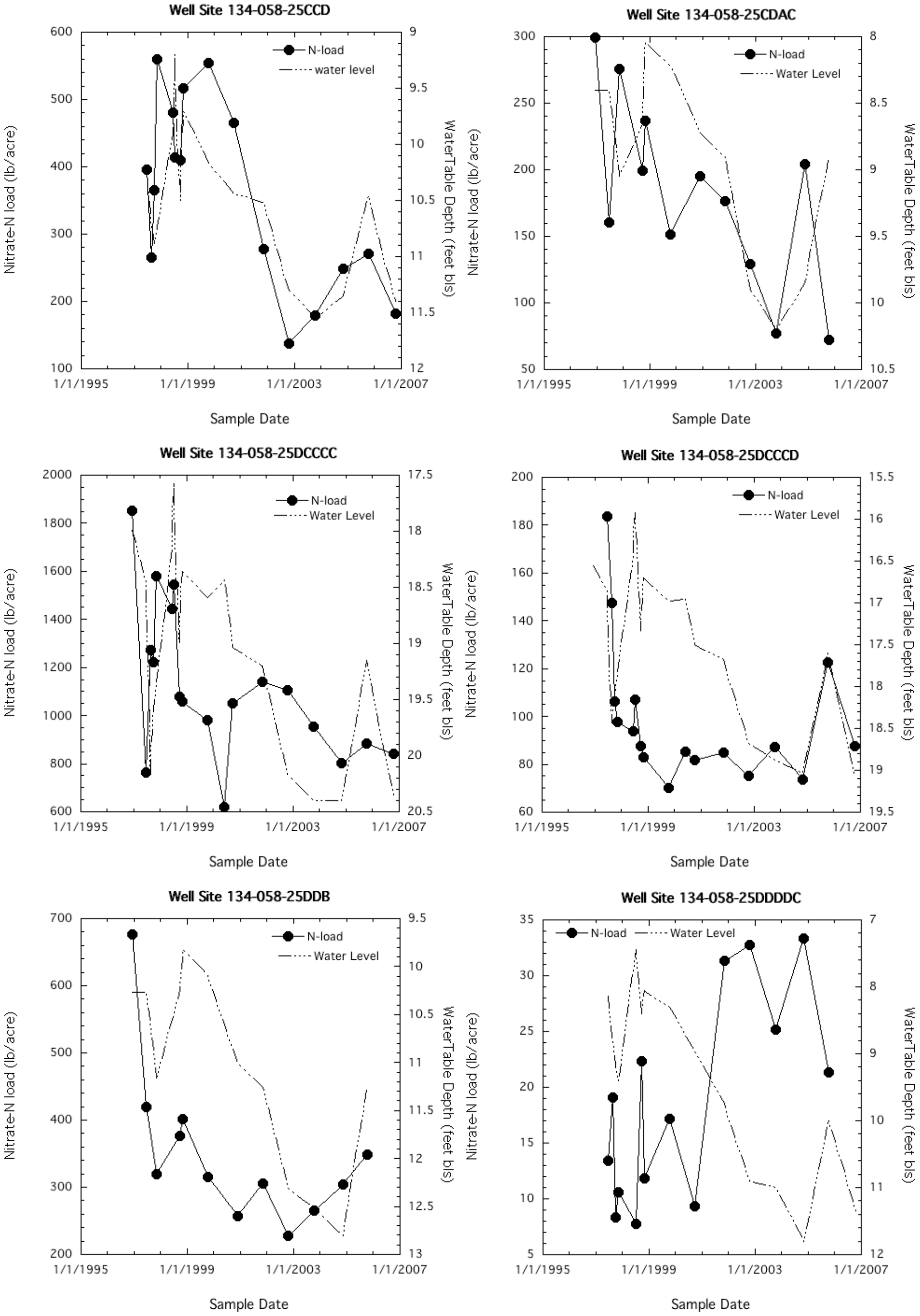

Figure 45. Temporal distribution of nitrate-N loads for well sites located in Section 134-058-25.

Because of large variability and close inter-proximity of the well sites along the south section border, we suspect that the largest local loads at -25DCCCC, which are about 3x the other largest load estimates, may have been caused by local point-source events, such as a fertilizer spill. This indicates that the main loading events likely preceded the period of measurement (post 1996), probably beginning during the wet period from 1993 to 1996, with some later loading from the wet spring of 1997.

PMCI Indices on Section 134-058-25

PMCI indices (Fig. 46) for two of the six well sites were initially at low levels (< 5 mg/L, based on an EPA-MCL of 10 mg/L for nitrate as N) and remained so throughout the measurement periods. Low PMCI sites included the well-site at the center of the southwest quarter pivot (-25CDAC). PMCI values included effects of both loads and saturated thickness. Thus, a thicker portion of the aquifer would have a lower index for the same nitrate-N load, and a thin aquifer section would be highly influenced by a relatively small load. At the end of the 10-year measurement period, four of the six sites were below, or at least fluctuating near a PMCI values of 10 mg/L, and all having large initial values had decreased to about 1/3 of their initial values.

An irrigation well (-25DCC), screened at 60-75 ft. bls, was located in the southwest corner of Section -25D, and near the monitoring well nest at -25DCCCC(Fig. 25). Long-term (since 1976) background Nitrate-N concentrations were approx. 1 mg/L, but increased to about 5 mg/L between 1990 and 1996, likely caused by the shift to a wet climate with large precipitation in 1993. The maximum mixed concentration of about 8 mg/L occurred following the 1997 large snowmelt events. Pumping of the irrigation well would serve to mix and integrate highly variable nitrate-N concentrations characterized by PMCI for six nearby well sites (Fig. 46). Five of the six well sites indicated an increase in nitrate-N, similar to the irrigation well, following 1997, and final (post 2001) nitrate-N values were similar, in aggregate, to the concentration of the irrigation well.

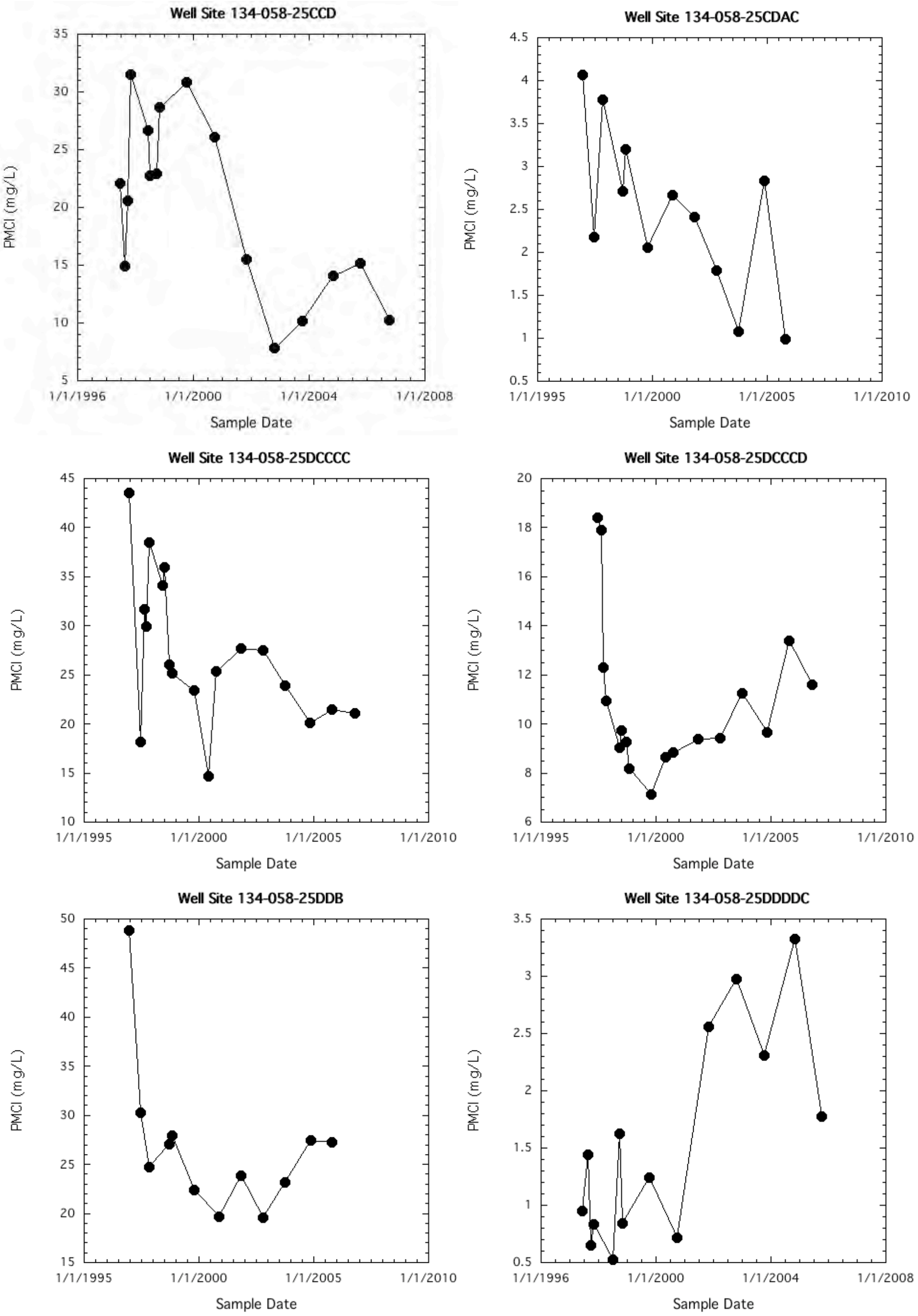

Figure 46. Temporal distribution of Potential Mixed Concentration Index (PMCI) for well sites located in Section 134-058-25.

Vertical Stratification of Nitrate Loading in 134-058-25

While total nitrate-N loads decreased at all sites, only two exhibited consistent decreases in nitrate concentrations in the shallowest wells of the nests (Fig. 47). These were -25CCD and 25CDAC. Others maintained similar overall concentrations in the shallow zone. The decreasing loads occurred primarily in the lower aquifer, as shown for two sites on Fig. 48. The evidence of initial but non-sustained deep nitrate penetration supports the hypothesis that large contamination events preceding the measurement period caused the main loading event(s), and that the measurement period was primarily a period of recovery in the deep aquifer, while the surface layer continued to receive leached nitrate.

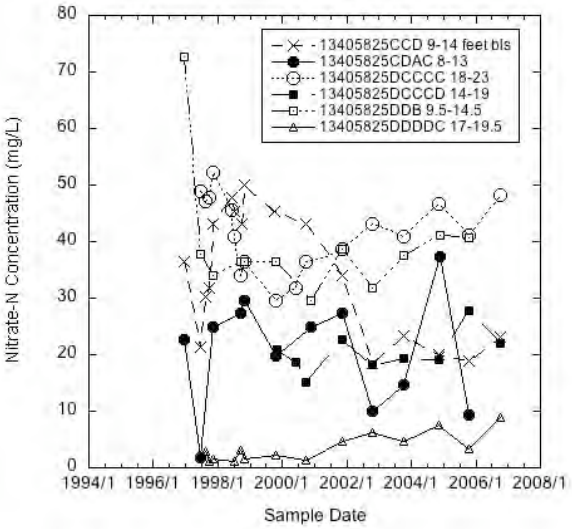

Figure 47. Nitrate trends in shallow wells on 134-058-25.

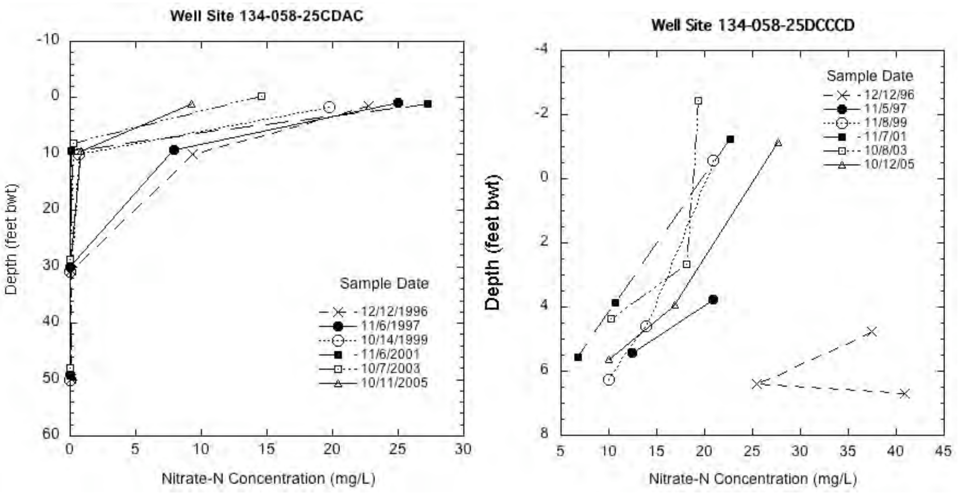

Figure 48. Vertical distribution of nitrate concentrations on well sites 134-058-25CDAC (left) and -25DCCCD (right).

Causes of Nitrate Dissipation in 134-058-25

Isotopic analysis (^{15}N and ^{18}O) for two of the sites (-25DCCCC and -25DCCCD) and at four other locations (in other portions of the aquifer) indicated that denitrification is occurring. In fact, the largest ^{15}N occurred in the well nest (-25DCCCC) with the largest nitrate concentration. Isotopes further indicated that similar denitrification with depth relationships applied broadly for the aquifer (Fig. 19).

Denitrificaton requires reducing conditions. DO fluctuated between approximately 2 and 4 mg/L at 5 to 10 feet bwt (Fig. 49). Limited data indicated that within 20 feet bwt DO was predominantly below 2 mg/L. One site (-25DDDDC) with the shallowest water table (7 to 12 feet bls) maintained DO near 1 mg/L. The depth of low DO and effective denitrification may be affected somewhat by the coarseness of the material. Oberdorfer and Pederson (1985) have suggested that, because bacteria lodge and reside in tighter grain environments, rather than in open large pores, reducing conditions may be present in the microenvironment, such as in the corners of sand and gravel grain, or in small local clay lenses. Thus, denitrification may occur even where the predominant characteristic DO is somewhat higher. The DO conditions demonstrated for well sites on 134-058-25 should be suitable (although not clearly ideal) for at least periodic denitrification.

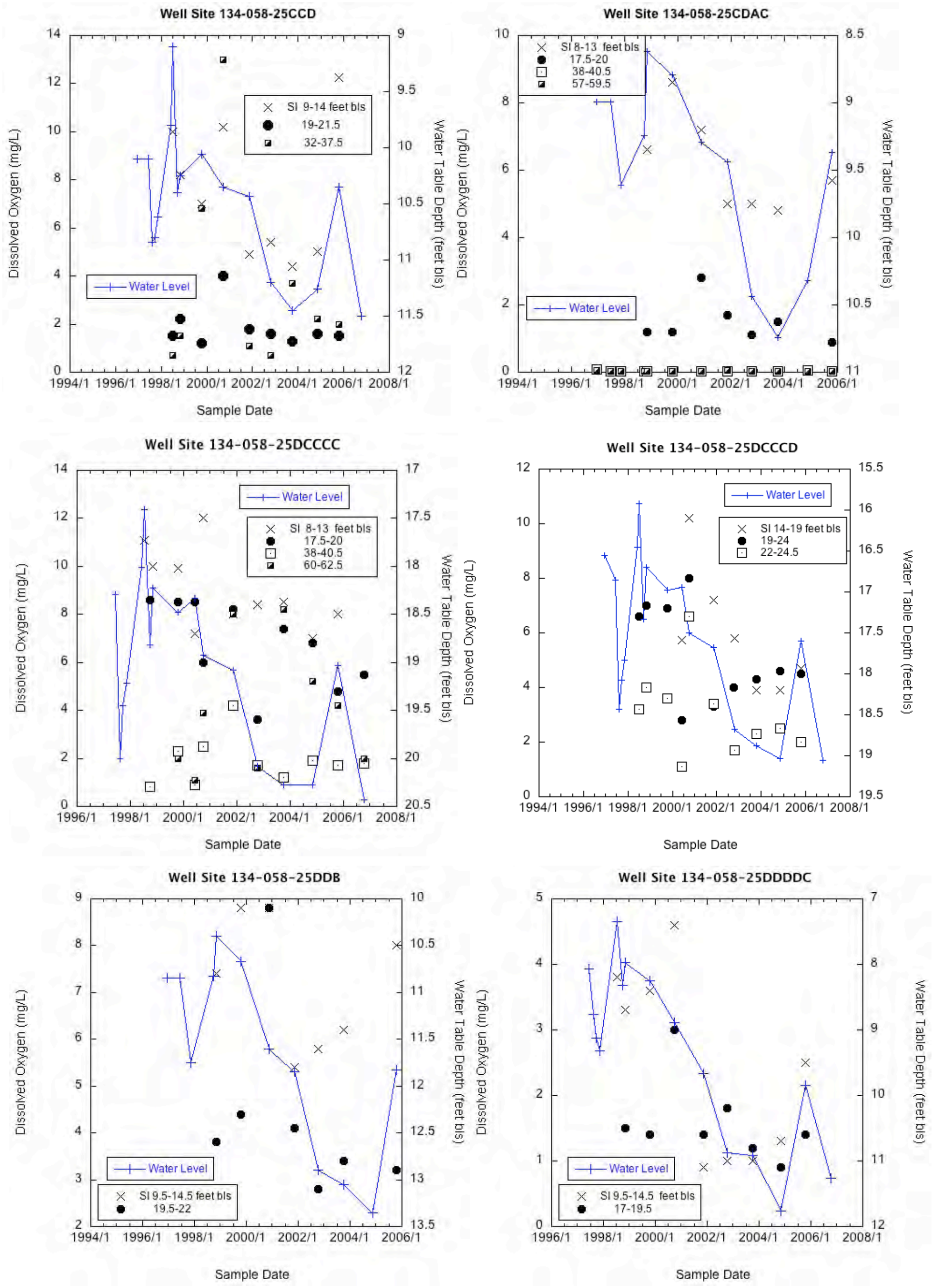

Figure 49. Temporal distribution of dissolved oxygen for well sites located in Section 134-058-25.

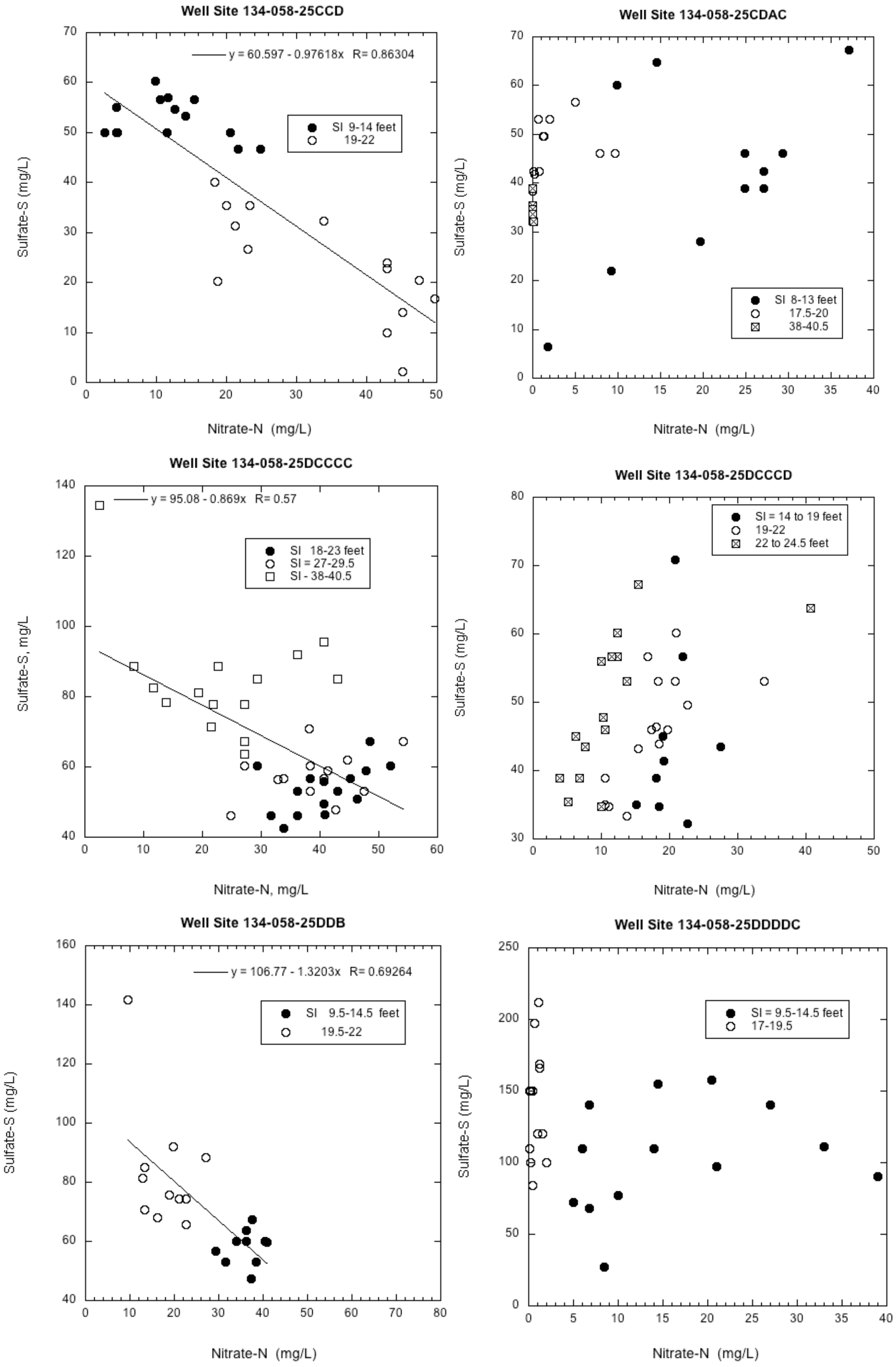

Figure 50. Sulfate-S vs. nitrate-N concentrations with depth.

Electron donors for denitrification have not been clearly identified, although work by Dr. Korom and his students (Report to the North Dakota Department of Health, dated August 7, 2002) have indicated that organic matter, inorganic sulfide, and reduced iron are common donors in the soils of eastern North Dakota and western Minnesota. Inverse stratification of sulfate and nitrate (increasing sulfate with depth corresponding to decreasing nitrate) is exhibited on all sites (Fig. 50). On three of the sites (-25CCD, -25DCCCC, and -25DDB) the inverse relationship is highly correlated across depth measurements, with coefficients ranging from about 0.9 to 1.3. The stoichiometric expectation for combined pyrite iron and sulfide as electron donors would be 1.63. Given the complexity of the field environment, which includes periodic refreshment of nitrate and periodic deeper influx of DO, which would also oxidize reduced sulfur and iron, the coefficients are reasonably close to the stoichiometric expectation.

The other three sites (-25CDAC, -25DCCCD, and -25DDDDC) are more complex, with greater variability of both sulfate-S and nitrate-N, so that inverse sulfate-S and nitrate-N are not highly correlated. However, the upward shift of sulfate-S with depth and with decreasing nitrate-N is clearly evident in the pattern of data clusters. One site (-25CDAC) exhibits a bimodal sulfate-S vs. nitrate-N relationship. These data have a strong direct (positive coefficient) correlation within the upper layer, likely caused by companion leaching from the overlying vadose zone, and pyrite oxidation with depth. Lacking data on the mineral content of aquifer strata, the actual electron donor cannot be positively identified. The upward shift of sulfate with depth could be caused by direct oxidation with periodic DO influx, and greater retained reduced sulfur substrate with depth. However, the repeated examples of strong inverse correlation with nitrate-N between depths, and supporting isotopic evidence of denitrification with depth support the contention that autotrophic denitrification employing reduced sulfur as an electron donor is likely occurring and contributing to both denitrification and sulfate generation. The general correspondence of dissipating nitrate-N loads and declining water tables (Fig. 49), combined with the observed sustained, or rapid recovery of low DO in the deeper strata within 15 to 20 feet of the water table (Fig. 49), indicates that the low DO is governed by the presence of a mineral reducing layer, and that declining water tables likely enhance nitrate dissipation by constricting the oxidized zone and drawing nitrate loads more closely to the reduced zone. Finally, decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management following 1996.

Contamination Status of Individual Well Sites in 134-058-25

- Well site 134-058-25CCD initially had a high nitrate-N load but decreased to a sustained moderately-high level. Trends for PMCI indicate that final "potential mixed" concentrations were at or below the EPA-MCL. This was affected by both relatively large saturated thickness and decreases in load. Nitrate-N loads appear to have stabilized with ongoing loading rates approximately matching dissipation rates. Slight improvement through decreased loading is desirable.

- Well site 134-058-25CDAC initially had a moderate nitrate-N load, but decreased to a very low level. PMCI in all cases were below 5 mg/L (half the EPA-MCL). This was affected by both low loads and relatively large saturated thickness. This site is in good condition.

- Well site 134-058-25DCCCC initially had a very high nitrate-N load. Loads remained very high, but decreased greatly to about a third of the initial loads and appear to have stabilized. PMCI indices decreased to about 2x the EPA-MCL. Isotopic evidence indicates that denitrification was definitely occurring on this site. Sustained loads and PMCI thus indicate that influx rates have approximately matched dissipation rates. PMCI are somewhat dampened by a moderate (approx. 40 feet) saturated thickness. Because of exceptionally large local loading, and much lower local loading in near proximity, a localized point source, perhaps a previous fertilizer spill, may have occurred at this location. Deep penetration of nitrate at this site would have been enhanced by drawdown from the irrigation well at -25DCC. Large improvement is desirable on this site.

- Well site 134-058-25DCCCD initially had a moderate nitrate-N load and decreased to a low load and apparently stabilized. The PMCI was initially about 2x the EPA-MCL and decreased to fluctuating within +/- 2 mg/L of the EPA-MCL. Isotopic evidence indicates that denitrification is occurring on this site, so that stabilization infers ongoing low-level loading. The marginally high PMCI were partially caused by the thin (7-to 10-ft.) saturated thickness. Slight improvement through decreased nitrate loading would be desirable on this site.

- Well site 134-058-25DDB initially had a high nitrate-N load, then decreased to a moderate level and stabilized. The PMCI was initially very high at about 5x the EPA-MCL, and decreased to a relatively high (2x the EPA-MCL) level and approximately stabilized. The sustained relatively high PMCI is caused by the thin saturated thickness. Improvement of this site through decreased loading is desirable.

- Well site 134-058-25DDDDC initially had very low nitrate-N load, then increased to about 2x the initial load, but still remained low. The PMCI remained low (< 5 mg/L, or ½ the EPA-MCL) throughout the measurement period. This site is in good condition.

Nitrate Summary for 134-058-25

Nitrate-N loads on section 134-058-25 varied widely within relatively short distances. There is little evidence of accumulation or dissipation along the flow path toward Englevale Slough. More likely nitrate concentrations reflect local events, with some possible displacement and dispersion in the flow system. One site, in particular (134-058-25DCCCC), is suspected to have been affected by a local fertilizer spill or over application at some past time. A pattern of initial high nitrate-N concentrations and loads, and initially deeper penetration of N followed by later dissipation, indicate that large nitrate-N influx likely occurred before the period of measurement, possibly in the very wet years beginning in and following 1993, and were likely affected by the wet spring of 1997. Previous discussion of climatic variables indicates that nitrate-N loads were strongly affected by climate. Because of deep water tables, decreasing nitrate concentrations are likely caused by denitrification in the deeper aquifer. Correspondence of declining water tables with nitrate dissipation indicates that constriction of the oxidized layer above the mineral reducing zone may enhance denitrification. This is further supported by evidence of decreasing nitrate in deeper wells, while concentrations in shallower wells were sustained. Isotopic evidence, DO distributions, and inverse (and sometimes highly correlated) stratification of nitrate and sulfate with depth all support the theory that denitrification was the main cause of dissipation. Improvement has been substantial. Approximate stabilization of nitrate loads and PMCI indicate that recent dissipation rates are being approximately equaled by ongoing replenishment. PMCI indices of toxicological impairment are affected by both nitrate loads and local saturated thickness. They indicate that several sites were in good condition, but that further improvement, through decreased nitrate loading, is desirable.

Middle Englevale Aquifer (Township 133 N, Range 58 W)

Monitoring well sites in the middle portion of the Englevale aquifer (USBLM 133-058) consist of five sites in Section 25 (Fig. 51), and one site in Section 2 (Fig. 59).

Figure 51. Location of monitoring well sites on Section 133-058-25.

Location and Characteristics of Well Sites on 133-058-25

Section 25 of Township 133 N and Range 58 W (133-058-25 USBLM) is located about 6 miles south of the town of Englevale. A substantial portion of the section is occupied by the Englevale Slough complex, primarily in the southeast quarter section and the middle of the western half, which serves as a discharge area. Ground-water flow on the east half of Section 25 is southward. Saturated thicknesses vary over a total range of 24 to 54 feet, and generally thicken from west to east, and then decrease approaching the slough (Table 1). A generalized cross section for the middle Englevale aquifer is shown on Fig. 52.

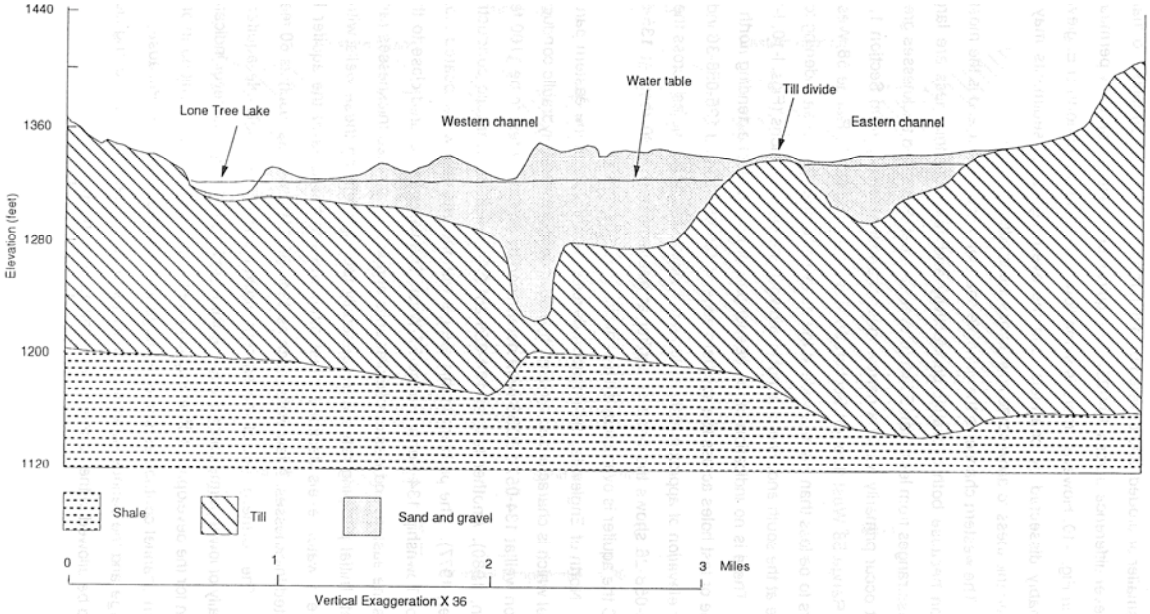

Fig. 52. Generalized cross section of the middle Englevale aquifer (from Cline and others 1993).

The monitoring wells are located in a dryland cropped area of the southwest quarter of Section 25, east of the slough (Fig. 52). Four of the wells (-25CCC, -25CCDC, -25CDCC, and -25CDDC) comprise a west-to-east transect from the southwest section corner to the border of the wetland. One well set (-25CBCC) is on the west field border about ¼ of a mile north of the southwest corner. The monitored dryland tract is bordered by irrigated tracts along the entire south, west and north borders, including southeast Section 23, east Section 26, northeast Section 35, and northwest Section 36. Monitoring wells toward the west are thus down-gradient of irrigated tracts, while those farther east would increasingly receive waters from under the non-irrigated grassland.

Depths to the water table (Table 1) vary from 14 to 23 feet in the western two well nests (-25CCC and -25CCDC) to 0.8 to 8 feet on the two well sets (25CDCC, and -25CDDC) approaching Englevale Slough. Soils of the western two well nests were mapped as Sioux-Renshaw series, both Hapludolls, which are seasonal recharge areas with deep water tables (Seelig and Richardson 1994). The eastern two well nests were of the Divide series (-25CDCC) and borderline between the Divide and Arveson series (25CDDC). Both of the latter series were of the Calciaquoll Great Group taxa, and therefore can function as seasonal recharge and discharge areas, but with the cumulative character of a mildly expressed net discharge area.

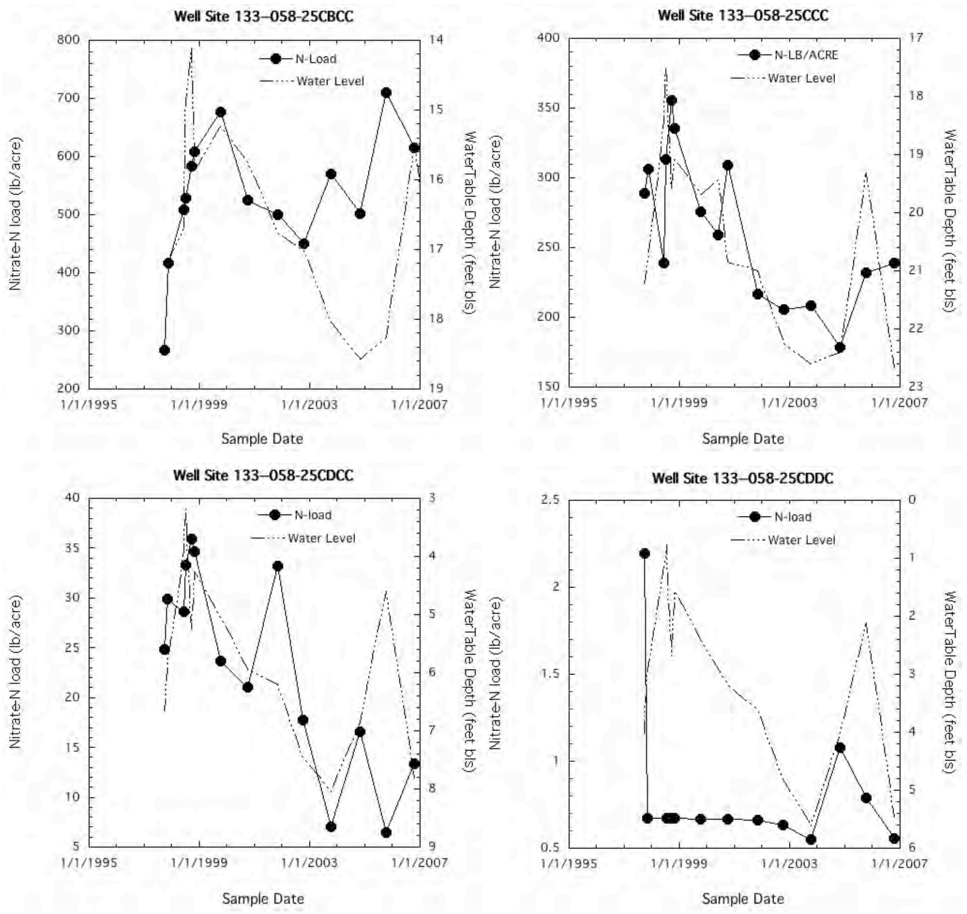

Figure 53. Temporal distribution of nitrate-N loads for well sites located in Section 133-058-25.

Nitrate-N Loads in Section 133-058-25

Nitrate-N loads vary widely both spatially and temporally, from negligible to local equivalents as high as 450 lb./ac. A summary of nitrate-N loads for Section 133-058-25 is shown on Fig. 53. Several observations of general trends can be made. These are:

- Nitrate-N loads varied directly with water table, increasing with rising water tables, and decreasing with shallower water tables.

- Three of the four well sites exhibited substantial net decreases in nitrate-N loads over the 10-year measurement period. The exception was the well-site located in the western field border near the center of the southwest quarter (-25CBCC) which lies closest to, and directly down-gradient of an irrigated field border, and which has the least buffer distance from the irrigated field. Nitrate-N loads on one well site (-25CCDC) were not calculated because of the large depth interval between the deep and shallow wells.

- The nitrate-N loads on the south-border transect decreased exponentially along from west to east toward the slough, with median values of 259 lb./ac. (-25CCC), 24 pounds-per acre (-25CDCC), and 0.7 pounds-per acre (-25CDDC) successively.

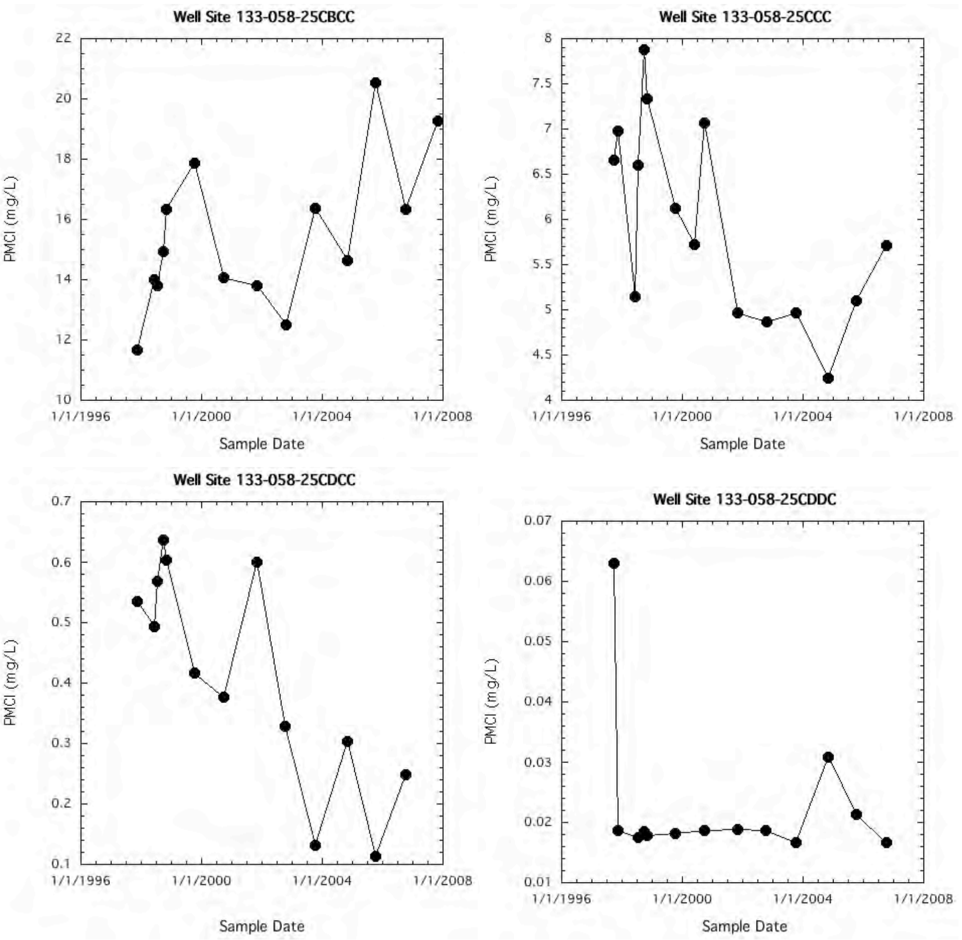

Figure 54. Temporal distribution of Potential Mixed Concentration Index (PMCI) for well sites in Section 133-058-25.

PMCI Indices on Section 133-058-25

PMCI indices (Fig. 54) for all of the well sites were very low to low, having median values ranging from 0 to 6 mg/L. All median values were below the EPA-MCL of 10 mg/L. The well nest having the largest load (-25CBCC), also had highly variable loads, fluctuating at times from as low as zero to as high as about 16 mg/L). The eastern-most well nest (-25CDDC) had virtually negligible nitrate-N loads and PMCI values at all times. PMCI are controlled by combined nitrate-N loads and saturated thicknesses. Both low loads and moderately large thicknesses contribute to low values at these sites.

Vertical Stratification of Nitrate Loading on Section 133-058-25

Unlike some other sites described in Sections 134-057-18 and 134-058-25, which maintained relatively large concentrations of nitrate in the upper aquifer and decreased mainly in the deeper aquifer, nitrate concentrations at all sites with decreasing loads in 133-058-25 decreased in the upper aquifer as well (Fig. 55). Time-sequential decreases in nitrate-N loading in the upper aquifer are shown for the eastern two transect well nests on Fig. 56. One reason is that significant nitrate-N penetration does not appear to have occurred beneath the surficial oxidized zone. One exception is well nest -25CCC where decreasing shallow nitrate (Fig. 56) was compensated by increasing deeper nitrate in 2006.

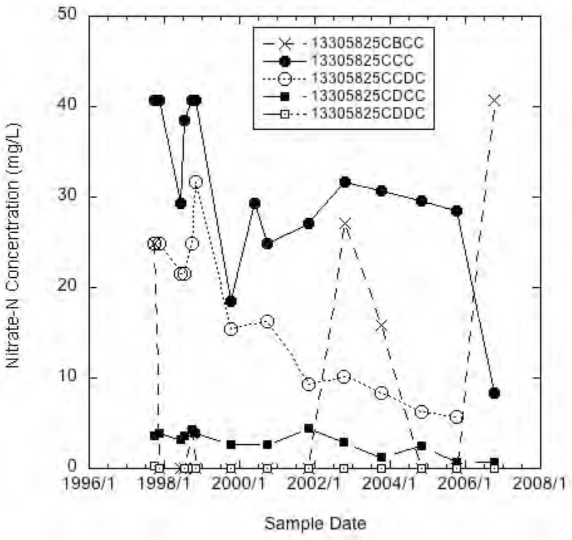

Figure 55. Nitrate trends in shallow wells on 133-058-25.

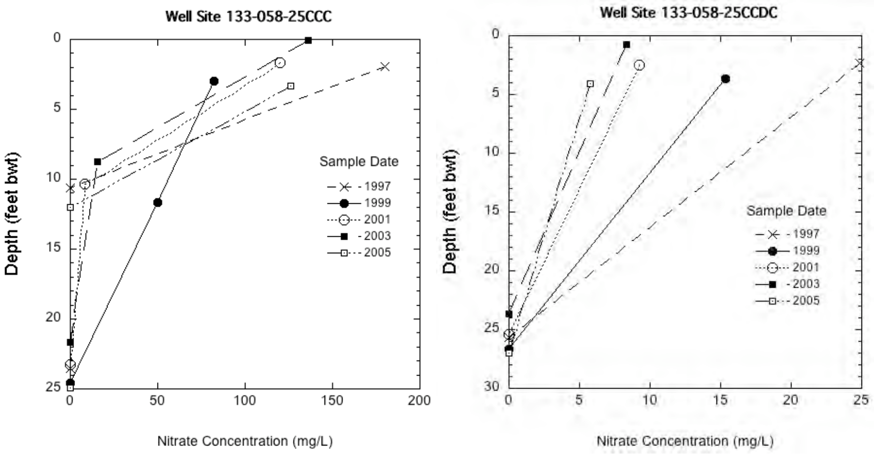

Figure 56. Vertical distribution of nitrate concentrations on well sites 133-058-25CCC (left) and -25CCDC (right).

Causes of Nitrate Dissipation on Section 133-058-25

Decreasing nitrate loads eastward on the transect was likely caused by distance from source areas. The western well nests (-25CBCC and -25CCC) are located immediately next to irrigated fields, and would receive southeastward flow from those fields within the prevailing flow system. Farther east (-25CDCC and -25CDDC), nitrate content would be buffered by flow beneath a grassland field. Dissipation through root withdrawal is infeasible on the western three wells (-25CBCC, -25CCC, -25CCDC) because water table depths indicate that the sites are uncoupled with respect to ET. Denitrification is a likely source of dissipation and was discussed in detail for tracts 134-058-25 and 134-057-18. Nitrate δ^{15}N values for 133-058-25CBCC increase with depth, and are elevated (+5.3, +7.37 SMAN) compared with minimum values (+3.76 to +3.8 SMAN). They also conform to the δ^{15}N vs. depth general relationship determined for the area.

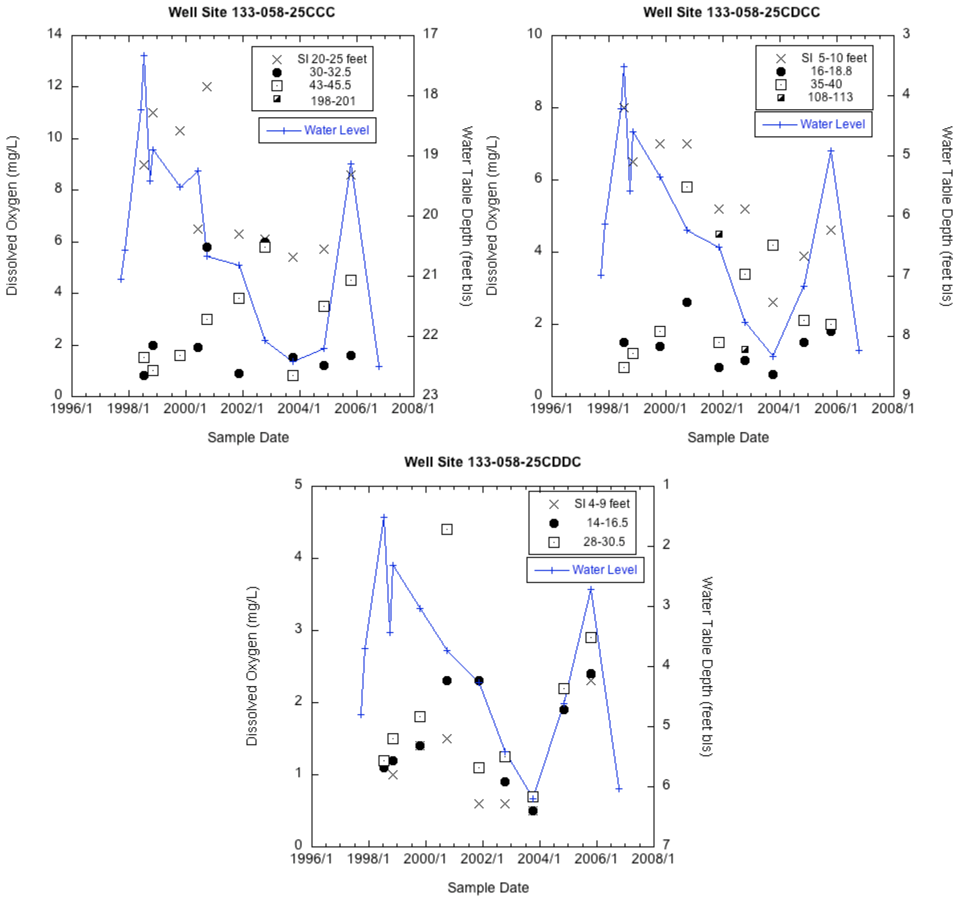

Figure 57. Dissolved Oxygen distribution with time and depth for well sites on 133-058-25.

The potential for denitrification depends on low oxidation-reduction state. Fig. 57 shows the DO for all depths at three sites along the west-east transect. In the deeper water-table locations (-25CCC and -25CDCC), DO for the shallowest wells increased with the rising water table, indicating oxygenation with recharge waters. Deeper wells at 10 to 20 feet below the water table, however, sustained low DO values except for brief periods following recharge events. This was likely caused by mineral-induced chemical oxidation demand from retained reduced minerals below the oxidized zone. The DO in the deeper wells did not vary widely with water table depth. For the site bordering the Englevale Slough (-25CDDC) DO was in the lower range (all below 5 mg/L and most below 3 mg/L) for all depths and times, including the shallow wells with SI at or near the surface of the aquifer. This may indicate a reducing environment in the vadose zone above the water table, and may be influenced by the organic carbon as an electron donor. Generally, DO should be sufficiently low to allow for denitrification within 10 to 15 feet of the water table at all sites.

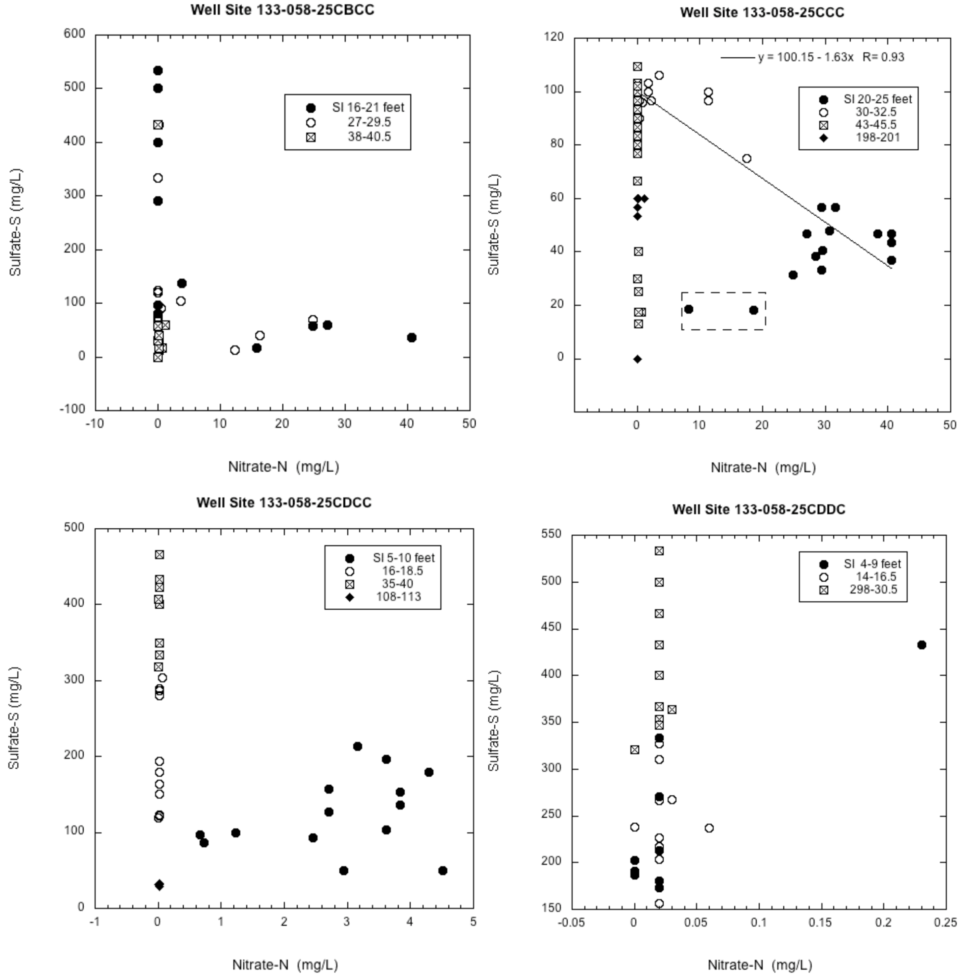

Figure 58. Sulfate-S vs. nitrate-N distribution with time and depth for well sites on 133-058-25.

The contribution of autotrophic denitrification cannot be determined for -25CBCC where surficial sulfate-S vs. nitrate-N was highly variable, or -25CDDC where all nitrate-N values are very low at all depths. (Fig. 58). A general relationship of increasing sulfate-S vs. nitrate-N with increasing depth is evident for -25CDCC. If two values are excluded (both shown in the dashed box on Fig. 58 were concurrent with large recharge and rising water tables), the sulfate-S vs. nitrate-N with depth at -25CCC was highly correlated with a coefficient of 1.63. This is nearly identical to the stoichiometric expectation of sulfate-S production from nitrate-N reduction using pyrite-S and Fe(II) as electron donors (Eq. 2). Because of the depth of the water table, autotrophic denitrification likely predominates in ground water near the western borders of the section. Nearer the slough complex, shallower water tables, which seasonably approach land surface, likely cause an increase in organic carbon from topsoil and subsoil sources. Enhanced carbon sources and a shallower water table may increase biological oxidation demand nearer the surface and enable heterotrophic denitrification, or under some conditions, non-assimilative nitrate reduction (to ammonium). The shallow water table may also enhance root uptake. Heterotrophic processes likely contribute to the near-complete removal of nitrate from the flow system at -25CDDC.

The conformance of nitrate-N loads to water levels [decreasing load with increasing water-table depth (Fig. 53)] may be caused by constriction of the oxidized zone above a reducing mineral layer, as discussed in previous (northwest and northeast) report sections. Finally, decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management following 1996.

Contamination Status of Individual Well Sites in 133-058-25

Using the PMCI as an indicator of contamination status, only one of the well sites measured (-25CBCC) has periodic nitrate-N concentrations approaching the EPA-MCL, and the median value on this site is well below levels of toxicological concern (Table 1). The other three sites analyzed (-25CCC, -25CDCC, and -25CDDC) all have sustained PMCI well below regulatory drinking water standards.

Nitrate Summary for 133-058-25

Nitrate-N loads for 133-158-25 were moderate to low, and decreased systematically along the flow path from source agricultural areas west of the measured sites to the Englevale Slough complex. Contamination status with respect to regulatory standards, as evaluated using PMCI, was low to very low for all sites. Nitrate ^{15}N data indicated that denitrification was occurring. DO was generally sufficiently low to allow for denitrification between 10 to 20 feet below the water table, and at one site (-25CDDC) very near the water table itself. Sulfate-S vs. nitrate-N data distributions with depth indicate increasing sulfate-S vs. nitrate-N on two sites. The relationship on one site (-25CCC) was highly correlated and corresponds closely with the stoichiometric expectation for nitrate reduction using pyrite iron and sulfur as electron donors. Near the Englevale Slough, shallower water tables likely contribute to reducing conditions, enhanced dissolved carbon as an electron donor, and root extraction.

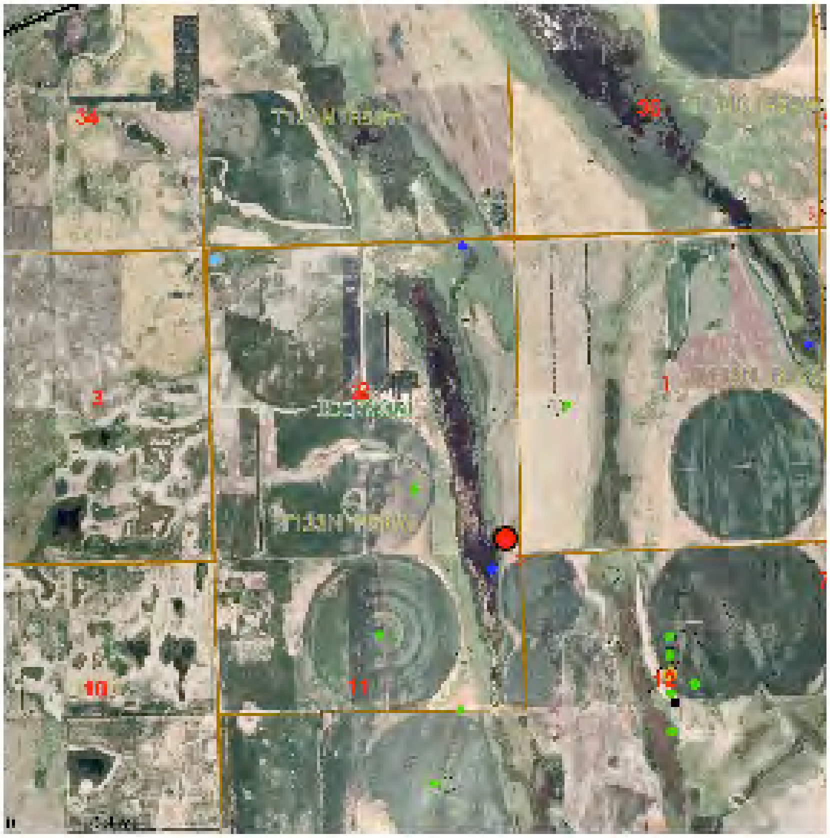

Figure 59. Location of the monitoring well site on Section 133-058-02.

Location and Characteristics of Well Sites on 133-058-02

Well site 133-058-02DDD is located about two and a half miles south, and a mile west of Englevale (Fig. 59). It is located in a non-irrigated tract near the eastern border of a wetland associated with the Englevale Slough complex. Irrigated tracts are located directly south of the well nest, but the local piezometric gradient is oriented generally toward the southwest so that the main nitrate sources should be non-irrigated tracts to the northeast of the site. The water table varied from about 15 to 19 feet bls. The soil series is mapped either to the Sioux-Renshaw complex, or a Renshaw loam, depending on the precision of the mapped border. These mapping units, both predominantly Hapludolls, are characterized as local seasonal and net recharge areas, which is consistent with the water-table depth. The aquifer was relatively thin, varying from about 17 to 21 feet.

Nitrate-N Loading and PMCI at Well Site 133-058-02DDD

The nitrate-N load varied from moderate to very low (Fig. 60). Higher loads occurred at the beginning of the 10-year monitoring period. Declining nitrate-N load occurred consistently over the measured period, and the final load was insignificant. The period of declining load corresponded to the period of falling water table.

The PMCI (Fig. 60) varied from slightly above the EPA-MCL of 10 mg/L to very low. The median PMCI was 7 mg/L, but consistent down-trending resulted in a final value of less than one mg/L with no indication of increasing contamination.

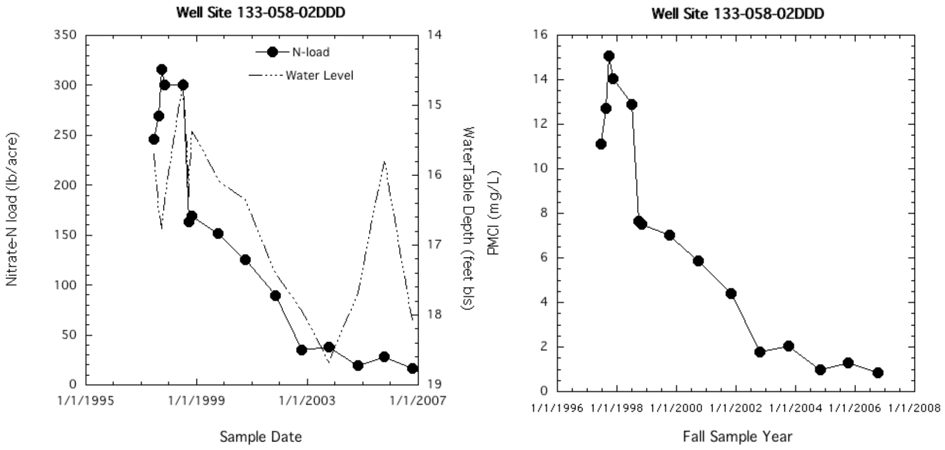

Figure 60. Nitrate-N load (left) and PMCI (right) trends over time for well site 133-058-02DDD.

Vertical Stratification of Nitrate Loading in 133-058-02DDD

All nitrate in 133-058-02DDD was limited to the upper aquifer at all times. Nitrate dissipation occurred in the upper aquifer over the measurement period (Fig. 61).

Causes of Nitrate Dissipation at Well Site 133-058-02DDD

Dissolved oxygen was sufficiently low below the surficial layer of the aquifer that denitrification is plausible (Fig. 62). Sulfate-S vs. nitrate-N with depth indicated an inverse relationship, which is consistent with autotrophic denitrification (Fig. 62). As with other sites discussed, denitrification likely contributed to nitrate dissipation. A stable zone of depleted nitrate within 10 feet of the water-table surface, regardless of the water-table depths, further indicates that nitrate dissipation as well as DO may be controlled by a zone of reducing minerals beneath the surficial oxidized zones.

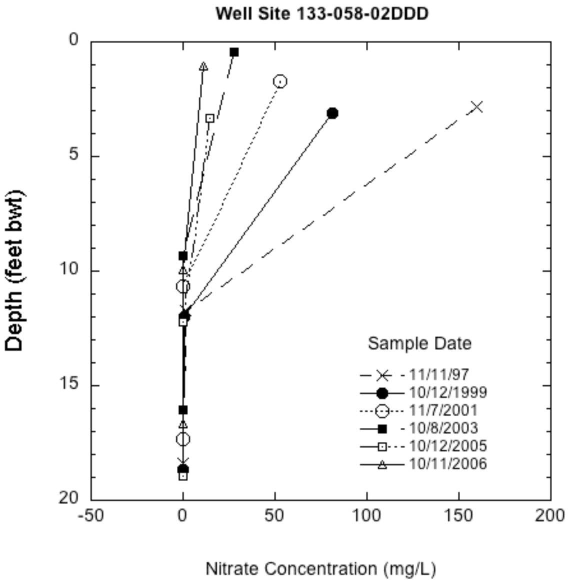

Figure 61. Nitrate concentration depth distribution with time for well site 133-058-02DDD.

Contamination Status at Well Site 133-058-02DDD

Well site 133-058-02DDD initially had somewhat high initial nitrate loads, when evaluated using the PMCI. However, consistent improvement and negligible final loads and PMCI indicate that this site is in good condition.

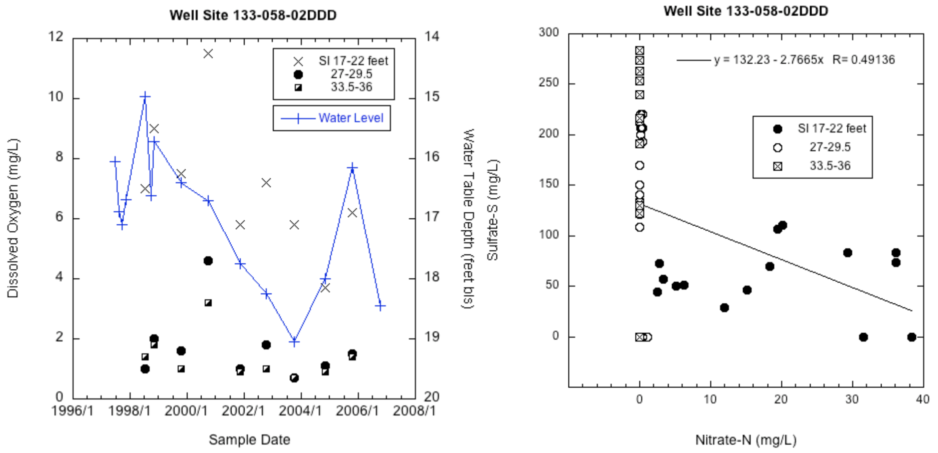

Figure 62. Dissolved Oxygen (left) and sulfate-S distribution (right) with time and depth for well site 133-058-02DDD.

Nitrate Summary at Well Site 133-058-02DDD

Nitrate was initially moderately high on this site, indicating a contaminating event that occurred prior to the monitoring period, which began in 1997. This may have occurred in the wet period following 1993, or it may have occurred in the spring of 1997, which had an exceptionally wet spring. Concentrations and loads dropped consistently and were very low at the completion of the monitoring period. Remedial action beyond normal precautions in good nitrate management should not be necessary.

South Englevale Aquifer (Township 132 N, Range 58 W)

The southern portion of the Englevale aquifer, within the study area, consists of two main components. The western part of the aquifer, including Sections 133-058-36, and 132-058-02, -11, and -14 and other lands to the south, consists primarily of a southern extension of the western deep channel, but with some buried deeper sand and gravel units (Fig. 63). The eastern portion of the aquifer consists primarily of a confined channel, beneath an aquitard sufficiently leaky to support substantial pumping for irrigation. This portion of the aquifer underlies the western halves of Sections 133-057-31 and 132-057-01. A generalized cross section for the south Englevale aquifer is shown on Fig. 64.

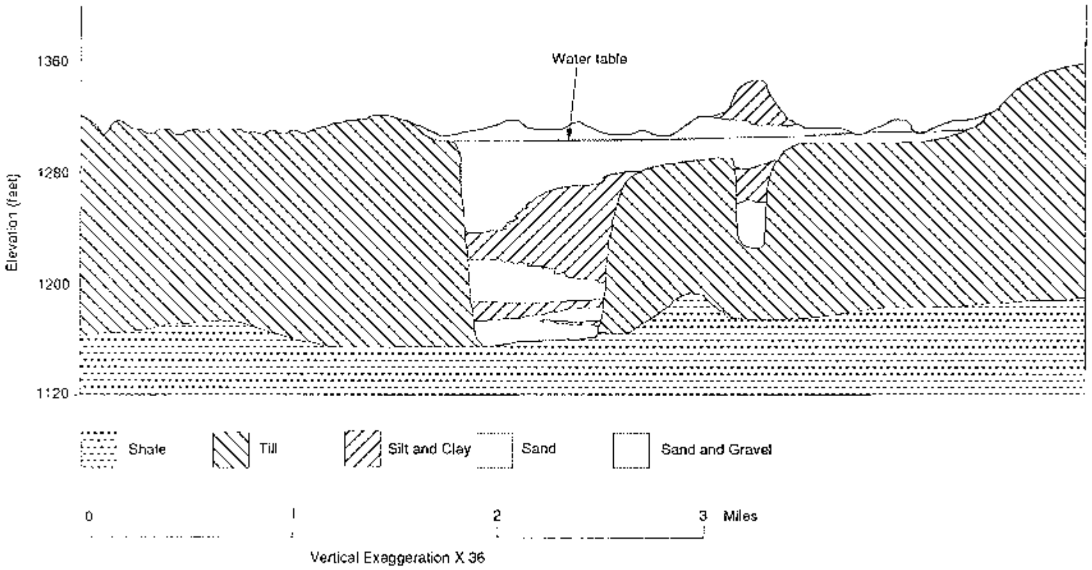

Figure 63. General cross section (left to right = west to east) of the south Englevale aquifer (From Cline and others, 1993).

Monitoring well sites in the southern portion of the Englevale aquifer (132-058) consist of two observation well sites and three irrigation wells in Section 1 (Fig. 64), and one observation well site each in Sections 13 and 35 (Fig. 71).

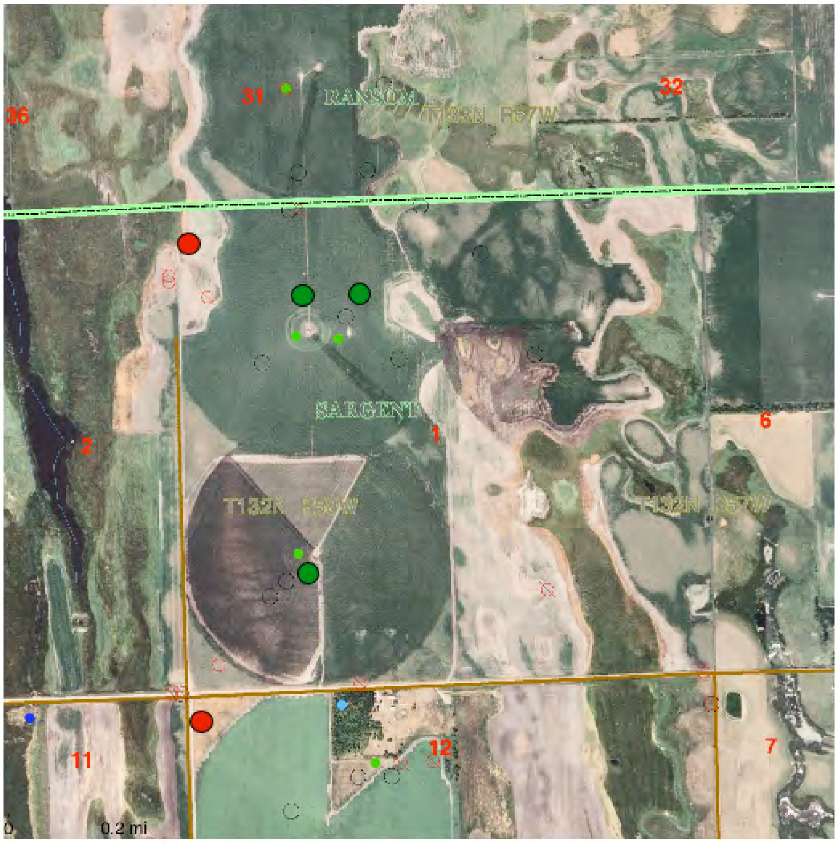

Figure 64. Location of monitoring (red) and irrigation (green) well sites on Section 132-058-01.

Location and Characteristics of Well Sites on 132-058-01

Section one of Township 132 N and Range 058 W (132-058-01 USBLM) is in Sargent County, about seven miles south of Englevale, and is bordered on the north by the Ransom County line. It lies near the eastern boundary of the Englevale aquifer, and is bounded on the west by the Englevale Slough complex. The eastern half of Section 1 contains a substantial area of wetlands. Agricultural use consists of three center pivots, located in the NE, NW and SW quarter sections, and limited dryland farming in the SE quarter section. The aquifer in this area consists of an unconfined shallow unit to about 20-25 feet bls, and a deeper confined unit about 20-30 feet thick with an upper boundary at 50-60 feet bls. All irrigation wells are screened in the lower (confined) unit.

Observation well site -01BBC is located between the irrigated field in the northeast ¼ and an area of seasonal wetlands. Observation well site -01CCC is located in the southwest corner of an irrigated field. In addition, water samples were available from three irrigation wells located at -01BCAD, and -01BDBD in the northwest ¼, and -01CBDD in the southwest ¼.

All wells are located within an aquifer flow system that trends southward (Fig. 2). Aquifer materials are predominantly of very shaley (40 to 70%) coarse sand and gravel, overlain by a silty topsoil. Saturated thicknesses at monitoring well sites are moderate to somewhat thin, varying from 15 to 22 ft. (-01CCC) to 22 to 28 ft. (-01BBC) (Table 1). The median water-table depth at -01CCC was 14 feet. This is consistent with the local mapped soil series (Spottswood Loam) which is of the Hapludoll Great Group taxa, and is considered to be a seasonal recharge area with and predominantly uncoupled with the water table (Seelig and Richardson 1994). The median water-table depths at -01BBC was about 4 feet, with a seasonal water table near land surface. This water-table depth is consistent with the local mapped soil series (Glyndon Loam) of the Calciaquoll Great Group taxa, which exhibits both seasonal recharge and discharge, but has a predominant long-term characteristic of net evaporative discharge.

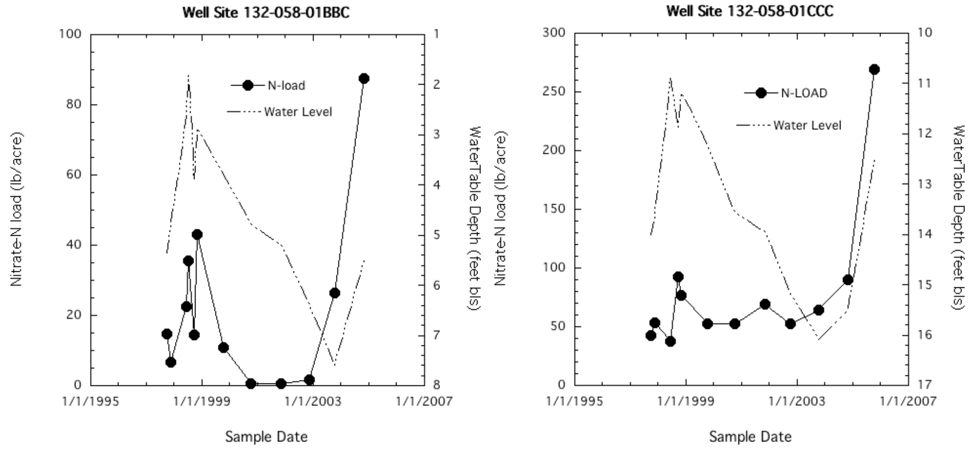

Figure 65. Nitrate-N load trends for Section 132-058-01 well nests.

Nitrate-N Loading on Section 132-058-01

Nitrate-N loads for both -01BBC and -01CCC, and for all irrigation wells were initially low to very low (Fig. 65). Loads for the observation wells tended to increase with increasing water table elevations, and decrease with lower water tables. Nitrate-N loads in observation wells began to increase substantially following 2002. The cause for the late increase is unknown, but may have been related to changes in land management.

PMCI in 132-058-01

PMCI values for all monitoring-network wells were initially very low (< 3 mg/L) and low (< 5 mg/L), and remained very low throughout most of the 10-year measurement period (Fig. 66). Even after load increases following 2002 the PMCI on site 01-BBC remained very low. Site -01CCC increased to above 10 mg/L following 2002.

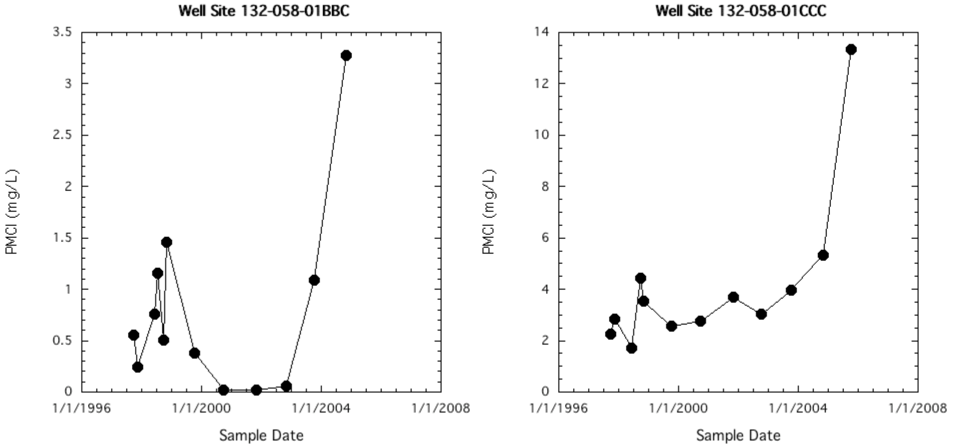

Figure 66. PMCI trends for Section 132-058-01 well nests.

Mixed concentrations for irrigations wells located in, or north of 132-058-01 are shown on Fig. 67. High nitrate was first observed in 1996 in an irrigation well a half mile north (133-157-31DCBB) which was screened in an aquifer unit confined beneath about 63 feet of sandy and silty clay. Maximum nitrate concentrations for other confined wells (-01BCAD and -01BDBD) were observed in June of 1997 following an exceptionally large spring melt (which caused record flooding on the Red River). The fast recovery of low concentration status (before 2000) in these wells indicates that contamination likely resulted from that large recharge event. The well having the largest nitrate response (-01BCAD) was confined locally beneath about 35 feet of till. However, the till-aquitard thickness is highly variable (e.g. thickness: 5 feet at -01CCAA, 22 feet at -01BDBD, 25 feet at -01CBDD). In this confined setting, direct local contamination from spills was not likely the cause of elevated detections. The causes were most likely related to the interaction of climate (large rains in 1993 and 1994, and a large snowmelt in 1997), and hydrologic factors (including: aquitard thickness, possible water-level thresholds for connection between shallow and deeper aquifer units that are climate-driven, and flow-system properties governing movement from the connected areas to the receiving wells).

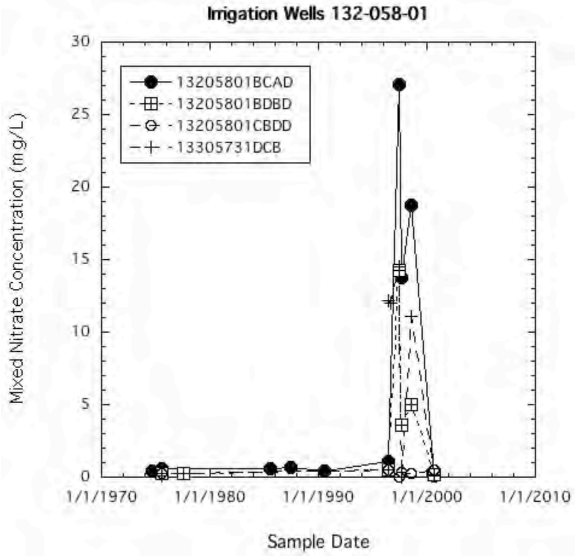

Figure 67. Mixed nitrate-N concentrations for irrigation wells 132-058-01BCAD, -01BDBD, -01CBDD, and 133-057-31DCB.

Some of the hydrologic factors likely governing the nitrate movement to and within the lower aquifer unit were: (1) Variable aquitard thickness, and leaky macro-scale properties of the aquitard, evident from the aquifer's ability to sustain large pumping from multiple wells; (2) the constricting effects of a relatively narrow (approx. ¼-mile wide) aquifer channel; and (3) high aquifer transmissivities, as evident from well recoveries and aquifer coarseness (gravel and cobbles) indicated in well logs. The high nitrate effects in the confined aquifer were ephemeral. Finally, decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management following 1996.

Vertical Stratification of Nitrate Loading in 132-058-01

All measurable nitrate was in the shallow well for each of the two nests. Trends of increasing nitrate influx into the shallow wells are shown on Fig. 68.

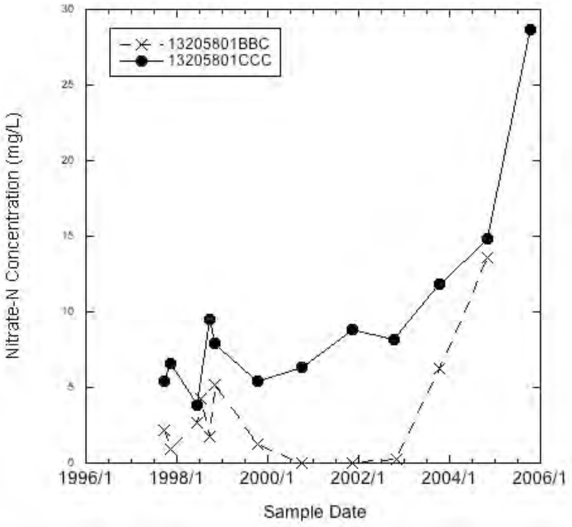

Figure 68. Nitrate (as nitrate) trends in shallow wells on 132-058-01.

Causes of Nitrate Dissipation for Section 132-058-01

DO measurements for all depths on site -01BBC were below 3 mg/L. The aquifer at this site should be sufficiently reducing to allow for denitrification (Fig. 69). There is no local evidence of increasing sulfate-S with decreasing nitrate-N (Fig. 70). However, with low nitrate loading rates, sulfate concentrations generated from nitrate would likely be masked by other sulfate sources. On this site, which is near a wetland complex, consistently low nitrate is likely caused by a combination of low loading and denitrification. Decreasing nitrate with the decreasing water table, which would thin the oxidized zone and draw nitrate within it into closer proximity with the reduced mineral layer, suggests a contribution of autotrophic denitrification. Organic carbon associated with the nearby wetland and the shallow water table on one site may also contribute to heterotrophic denitrification. On site -01CCC shallow wells had relatively high DO, but deeper wells maintained relatively low DO. There is no evidence of increasing sulfate-S versus decreasing nitrate-N with depth. Causes for dissipation on this site are somewhat speculative and based on known processes established elsewhere.

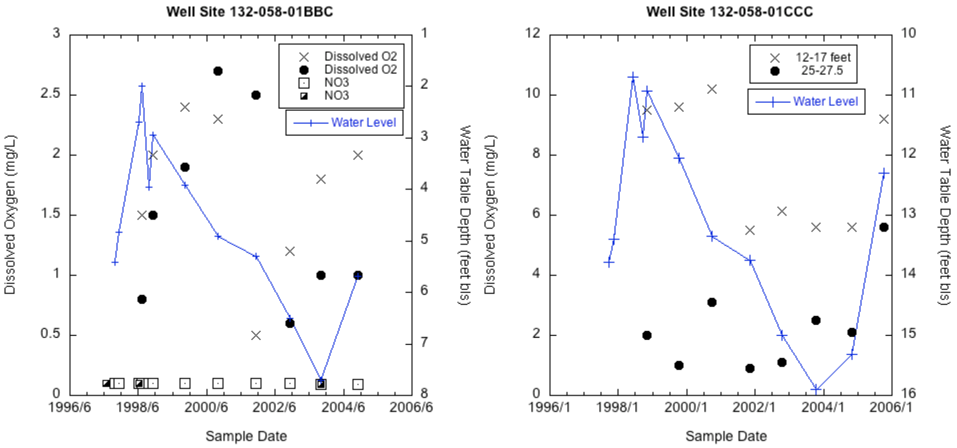

Figure 69. Dissolved Oxygen distribution with time and depth for well sites in 132-058-01.

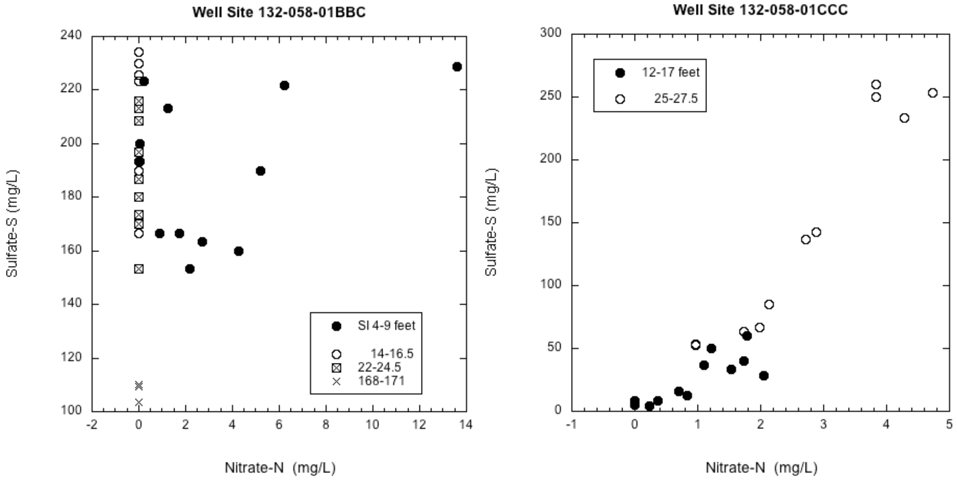

Figure 70. Sulfate-S vs. nitrate-N distribution with time and depth for well sites on 132-058-01.

Contamination Status of Individual Well Sites for Section 132-058-01

All three irrigation wells and the observation well at -01BBC had low loads and low PMCI, despite temporary periods of upward trends. These sites are generally in good condition. Well site -01CCC exhibited low loads and low PMCI throughout most of the 10-year measurement period, but were exhibiting increasing and high PMCI near the end of the measurements. While the long-term median PMCI is low, the late increasing trend should be monitored to assure that an ongoing pattern of contamination is not established. A decrease of nitrate-N at -01CCC would be beneficial.

Nitrate Summary for 132-058-01

Nitrate concentrations for observation wells and irrigation wells on 132-058-01 were generally low. Causes of low concentrations are speculative, but may include relatively low loading rates and heterotrophic and autotrophic denitrification in some areas. Increasing late trends in the observation wells are of concern if they continue, and should be monitored. Normal caution should be sufficient for ground-water protection from nitrate contamination in this area.

Figure 71. Location of monitoring (red) and irrigation (green) well sites on Section 132-058-13CCC and 132-058-35AAA.

Other Well Sites in the South Englevale Aquifer (On 132-058)

Two additional well sites in Township 132 N, Range 58 W are located at 132-058-13CCC and 132-058-35AAA (Fig. 71). These well nests are aligned on an approximate north-south transect with wells in 132-058-01 described above, and are spaced about 2 miles apart. Well site -13CCC is located about 11 miles south of the town of Englevale. It lies in the southwest (non-irrigated) corner of an irrigated quarter section, about a half mile northeast of a southern component of the Englevale Slough complex, named Bruns slough. The flow system is southwestward toward Bruns Slough. This site is neighbored by irrigated quarter sections on the NE, SE, SW and NE sides. Well site -35AAA is located about three miles farther south. It is situated approximately midway between, and slightly more than a quarter-mile distance from the southeast corner of Bruns Slough on the west, and the northwest corner of Big Slough on the east, and about a quarter mile from the wetland-complex that connects the two larger waterbodies to the south. It is neighbored by irrigated quarter sections on the NW and NE, and is situated within the flow system between those irrigated fields and the evaporative sinks in the slough complex to the south.

Both of the well nests have relatively deep water tables (8.8-13.1 feet bls for -13CCC and 15.14-19.6 bls for -35AAA). The area of well site -13CCC is mapped to the Spottswood loam soil series, while -35AAA is mapped to Gardena-Glyndon loams with a sandy substratum. The water-table ranges are consistent with Spottswood and Gardena series, which are Hapludolls and act hydrologically as seasonal and net recharge areas. The Glyndon soil, while present in the mapped area of -35AAA, is a Calciaquoll and would require shallower seasonal water table than that measured. Both sites should be characterized by local recharge, and by flowthrough of water from neighboring irrigated fields. Both sites have relatively large saturated thickness at about 50-54 feet, and 38-43 feet (Table 1).

Nitrate-N Loading in 132-058-13CCC and 132-058-35AAA

The nitrate-N loads on these two sites varies from very low to moderately high, with a maximum less than 500 lb./ac. (Fig. 72). The load under -13CCC began moderately high in 1997 and declined consistently to a negligible level over the 10-year measurement period. The load conformed directly to the water table, with highest loads occurring with the shallowest water table. This indicates that loading occurred during recharge, and that the recharge source was likely in close proximity to the wells. No load increase occurred under a mild recharge event which occurred in 2005. The load under -35AAA was moderately low in 1997 and increased consistently until 2002. The delay of peak recharge likely indicates a transient plume with a loading source more distant from the well site. A large and more immediate increase in load occurred with a smaller recharge event occurring in 2004-5. Nitrate sources on this site are highly variable and sporadic.

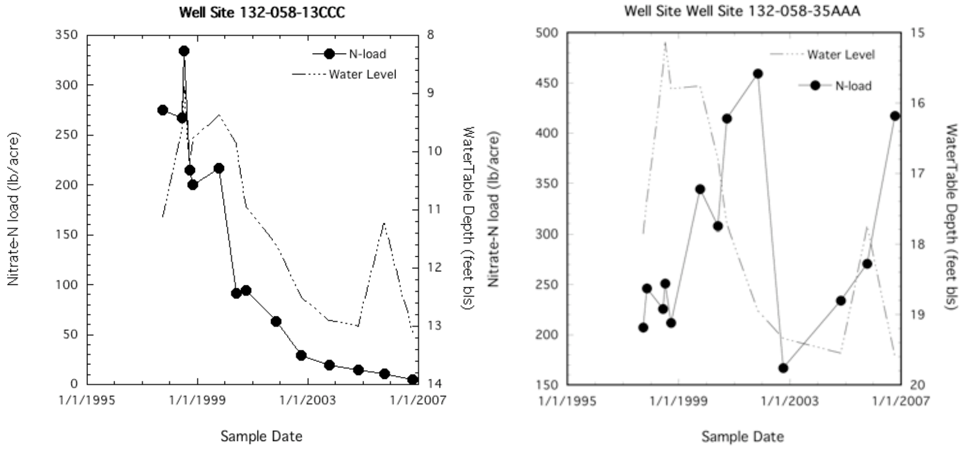

Figure 72. Nitrate-N load trends for 132-058-13CCC and 132-058-35AAA well nests.

PMCI Indices for 132-058-13CCC and 132-058-35AAA

Toxicological assessment using the PMCI (Fig. 73) indicates very low (< 3 mg/L) levels for -13CCC. Trends indicate sustained dissipation of nitrate. PMCI for -35AAA varies from low to four measurements near the 10 mg/L limit. However, the median value was 5.6 mg/L, which is relatively low.

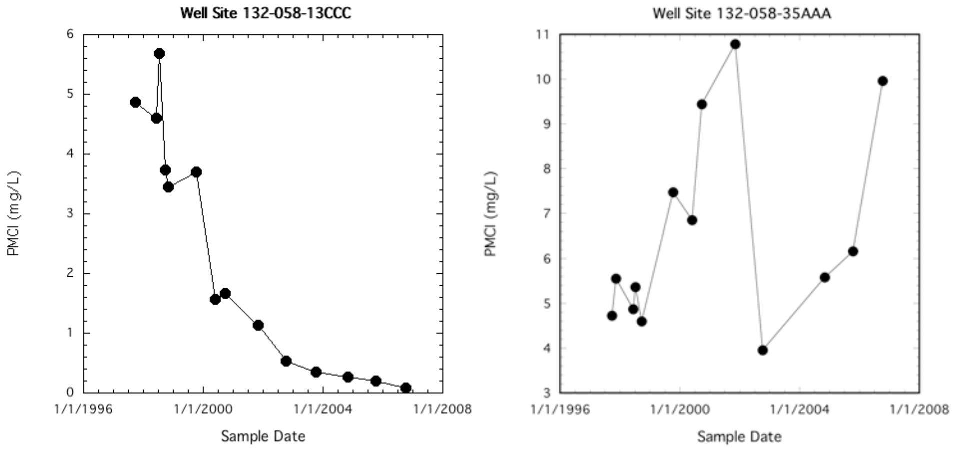

Figure 73. PMCI trends for 132-058-13CCC and 132-058-35AAA well nests.

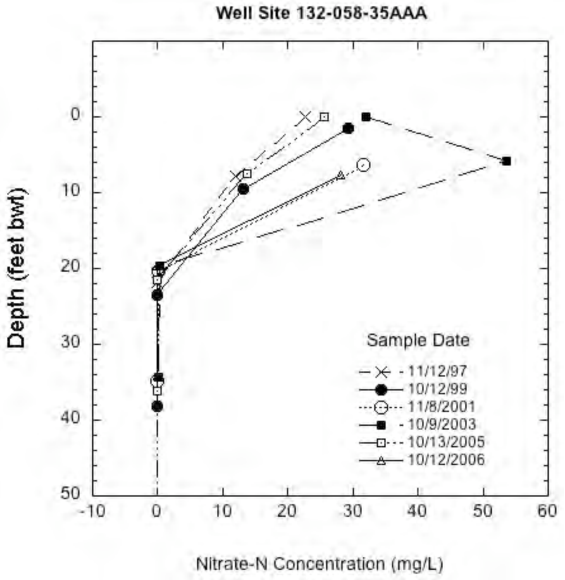

Figure 74. Vertical distribution of nitrate concentrations on well site 132-058-35AAA

Vertical Stratification of Nitrate for the 132-058-35AAA well nest

Nitrate was initially stratified in well nest 132-058-35AAA (Fig. 74). Although there was some fluctuation in nitrate concentrations, there were no significant trends of nitrate dissipation in the shallow unoxidized portions of the aquifer. Fluctuations of nitrate concentrations occurred as variable concentrations in the upper aquifer.

Causes of Nitrate Dissipation at 132-058-13CCC and 132-058-35AAA

For both sites DO below the surface layer should be sufficiently low to support denitrification (Fig. 75). DO increased sporadically following recharge events, but decreased quickly, despite a sustained shallow water table. Low DO on these sites occurred within 10 feet of the aquifer surface. This was most likely caused by the chemical oxidation demand of the minerals below the upper (oxidized) zone of the aquifer. This is further supported on well site -35AAA by the vertical nitrate-N profile, which indicates that the high-concentration zone of the upper aquifer is constricted between the water table and a stable extinction zone. Note that extinction zone depth did not change when the zone of high surficial nitrate moved downward with the declining water table in 2001 and 2006. Finally, decreasing nitrate-N loads and PMCI were likely also strongly affected by changes in nitrogen fertilizer management following 1996.

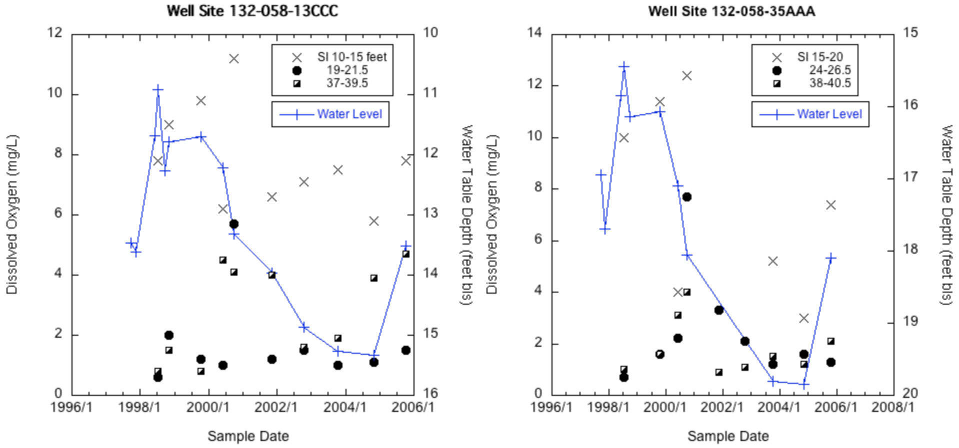

Figure 75. Dissolved Oxygen distribution with time and depth for 132-058-13CCC and 132-058-35AAA well nests.

General trends of increasing sulfate-S vs. nitrate-N with depth are discernible on both sites (Fig. 76). On -13CCC higher S with lower N with depth is discernible but qualitative, and a second trend (increasing sulfate-S vs. nitrate-N) is evident within the surface layer alone. This indicates that leaching of mobilized nitrate from the surface has a companion sulfur source, either as applied ammonium sulfate fertilizer, or as sulfate mobilized from evaporative concentrations in the soil profile as a "pass-through" source. At -35AAA the sulfate-S vs. nitrate-N was inverse and highly correlated from the surface to the neighboring low DO layer, and had a rate approximately half of that expected from autotrophic denitrification using a combined pyrite iron and sulfate source. These indicate that autotrophic denitrification may have contributed substantially to dissipation, and therefore to the variability of nitrate-N on this site.

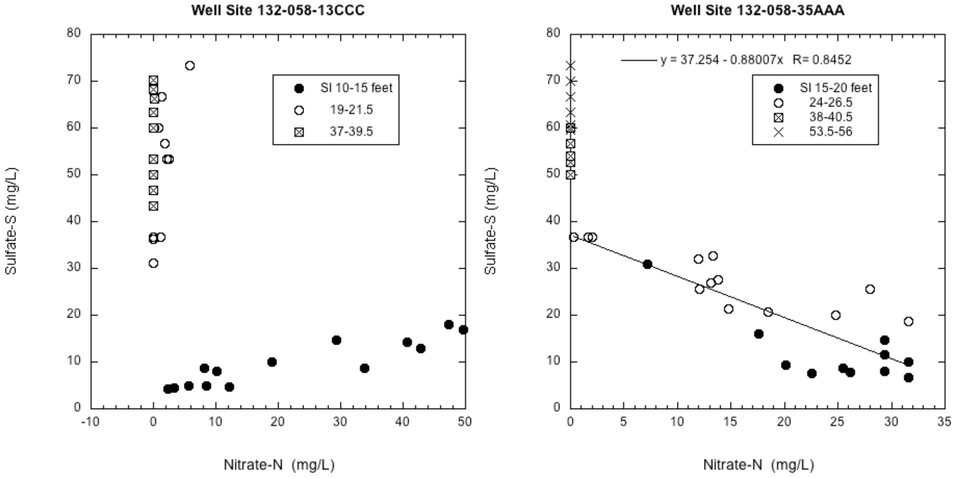

Figure 76. Sulfate-S vs. nitrate-N distribution with time and depth for well nest 132-058-13CCC and 132-058-35AAA.

Contamination Status for Well Sites 132-058-13CCC and 132-058-35AAA

Nitrate-N contamination for both well sites is relatively low and for the most part below levels of toxicological concern. Nitrate conditions are excellent at -13CCC. They are generally good at -35AAA, but because of variability some caution in maintaining low loads at this site is warranted.

Nitrate Summary for Well Sites 132-058-13CCC and 132-058-35AAA

As with sites in 132-058-01, nitrate-N loads and PMCI was mostly low to very low, with some short-term variation. Denitrification likely contributed to maintaining relatively low levels of nitrate. Remedial measures should be unnecessary. Some additional caution in the area of -35AAA is warranted. Normal caution in nitrogen management should be generally sufficient in this area.

CONCLUSION

Results of nitrate measurements from water samples collected from irrigation wells by the SWC in 1996 indicated that nitrate concentrations had increased substantially. Irrigation well samples collected from 1996 through 2001, from as many as 45 wells, had median concentrations two to three times the median of all samples collected from 1975 through 1995. Before 1996 nitrate-N was below 3 mg/L for all irrigation-well samples but one, and no samples exceeded 10 mg/L. Between 1996 and 2001 65% of the individual samples were less than 3 mg/L, 80% were less than 5 mg/L, and 96% were below the EPA-MCL threshold of 10 mg/L. An index of contaminant status based on time-composite median mixed nitrate-N concentrations and median nitrate-N loads for each irrigation well site between 1996 and 2001 indicated that the entire aquifer had very low (< 3 mg/L), low (<5 mgl), or moderately high (between 5 and 10 mg/L) contaminant status, with highest concentrations in Section 134-058-36 near Englevale. Most of the aquifer was mapped in the "very low" contaminant class. This sample set was poorly represented in the northeastern portion of the aquifer.

A supplementary well set consisting of nests of observation wells was constructed or enhanced in 1996 and 1997, and sampled through 2006. At varying times, as many as 30 observation-well locations were used to evaluate nitrate contamination based on estimated nitrate-N loads and a potential mixed concentration index (PMCI) designed to approximate the mixing effects of high-capacity wells. Time-integrated median PMCI for the observation well sites were generally greater than mixed concentrations from irrigation wells. Results indicated 75% of the well sites had time-integrated nitrate-N concentrations less than 10 mg/L, 50% were less than 5 mg/L, and 40% were less than 3 mg/L. The wider range of values compared with irrigation wells would be expected due to larger spatial and temporal integration represented in pumping wells and local removal of nitrate through pumpage, compared with highly localized spatial representation in observation-well samples. Also, observation well sites are more frequently located in thinner areas of the aquifer which have thinner unoxidized zones, and would therefore support less denitrification.

Nitrate-N dissipation with time was exponential, and therefore first-order with a time (and concentration) dependent rate constant. Average load dissipation rates were 4% per year for the mean, and about 8% per year for the median values. These are similar to dissipation rates measured for the Karlsruhe aquifer between 2000 and 2006, which were also first order and had an overall dissipation rate of about 6% per year.

The main cause of dissipation was denitrification. Nitrate was strongly stratified with depth, and was almost always fully dissipated within 10 to 20 feet of the aquifer surface. Nitrate ^{15}N was also stratified for water samples from several sites distributed over the aquifer. Composite ^{15}N increased with depth as a consistent exponential function of depth. This is consistent with a first-order decay with depth. The relative increase in nitrate ^{15}N with depth on each site was also strongly inversely correlated as a power function of the relative change in nitrate concentrations with depth for all sites combined. Nitrate ^{18}O also increased with depth. Nitrate ^{18}O was strongly correlated with ^{15}N with a linear coefficient of 0.485, almost identical to the expected (0.5) coefficient for denitrification. While specific electron donors for denitrification were not identified, ^{34}S and ^{18}O isotopic signatures for dissolved sulfate were consistent with (but not unique to) denitrification using a pyrite-sulfur source as an electron donor. Inverse stratification of sulfate with nitrate between the oxidized aquifer surface and the unoxidized zone was observed and documented on the majority of observation well sites. On some sites increasing sulfate with depth corresponded reasonably well with the stoichiometric expectation for reduction of nitrate using pyrite sulfide and iron as electron donors. It is, therefore, very likely that autotrophic denitrification was a strong contributor to nitrate dissipation, if not the dominant contributor.

For most sites, DO at 10 to 15 feet below the water table remained low, and temporary increases following recharge events were quickly dissipated. These indicate that DO below the oxidized zone is controlled by reducing minerals rather than oxygen diffusion limitations, and that the overlying oxidized zone is sustained because of the historical depletion of reducing minerals. It is thus likely that part of the climatic correlation with nitrate concentrations is caused by constriction of the oxidized zone with decreasing precipitation and recharge. The constriction causes increased mixing of nitrate within the reducing zone, enhancing its dissipation. If this is true, it would be predicted that precipitation in the future would again increase nitrate concentration, not only through increased loading, but also through attenuated dissipation in a thicker oxidized zone in the upper aquifer.

Changing agricultural practices has also likely contributed to decreasing nitrate concentrations and loads. Following first detections of elevated nitrate in 1996, many producers changed from spring pre-plant nitrogen applications to timed application through their irrigation systems. "Spoon feeding" nitrogen is a well known and accepted method for optimizing crop uptake of nitrogen, and likely contributed considerably to declining nitrate levels in the aquifer.

Finally, to assess the overall nitrate contamination status of the Englevale aquifer, it is reasonable to conclude that although a substantial increase in nitrate-N loading occurred following wet climatic events during the mid 1990s, most of the aquifer remains low to very low in contamination status, and concentrations have been decreasing, overall, during the post-1996 measurement period. A relatively small portion, consisting of about three to four quarter sections near Englevale, and about six to eight quarter sections in the north central portion of the aquifer, have high nitrate loads and exceed toxicological standards. These should be considered for enhanced nitrate management, and ongoing monitoring. Careful nitrate management should be exercised over all the aquifer to prevent future nitrate contamination.

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