Evaluation of Nitrate Sources Using Nitrogen-Isotope Techniques in Shallow Ground Water Within Selected Lake Basins in the Central Lakes District, Polk and Highlands Counties, Florida

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Abstract

Elevated nitrate concentrations are present in shallow ground water in selected lake basins in the Central Lakes District of Polk and Highlands Counties, Florida. Because there are no significant natural mineral sources of nitrate in Florida, the presence of nitrate in ground water is indicative of land use activity. Other factors that affect the concentration of nitrate in ground water are the rate of recharge, the concentrations of nitrogen species in atmospheric deposition, and the amount of dissolved oxygen in the ground water. A technique based on nitrogen isotopes was used to identify the likely sources of nitrate in ground water in the study area. Nitrogen isotopes in nitrate are distinctly different for organic (septic and animal waste) and inorganic (fertilizer) sources of nitrate.

Water samples collected from wells that tap the surficial aquifer system in the lake basins studied indicated varying concentrations of nitrate in different areas of the basins. Samples collected from wells in undeveloped land parcels had very low nitrate concentrations, less than 0.002 milligram per liter. The nitrogen-isotope ratios of nitrate in these samples ranged from +9.0 to +16.6 per mil and indicate that fractionation, probably of soil-derived nitrogen, has occurred. Water samples collected from wells in citrus land-use areas had the highest nitrate concentrations, ranging from 4.9 to 57 milligrams per liter. The nitrogen-isotope ratios for these samples ranged from -0.7 to +10.9 per mil, indicating that the nitrate is probably of inorganic (fertilizer) origin. In residential areas, nitrate concentrations ranged from less than 0.02 to 4.6 milligrams per liter and nitrogen-isotope ratios ranged from -6.8 to +13.4 per mil. These data indicate that the source of nitrate was either inorganic or organic, or a combination of both. In areas of mixed land use (undeveloped, citrus, and residential), nitrate concentrations ranged from less than 0.02 to 37 milligrams per liter and nitrogen-isotope ratios ranged from -7.0 to 15.3 per mil. The nitrogen isotopes were used in combination with ground-water head distributions, land-use information, and other geochemical data to better understand ground-water recharge, flow patterns, and chemical reactions that occur along ground-water flow paths.

INTRODUCTION

In recent years, the Central Lakes District of Florida (fig. 1) has experienced an increase in residential development. Increased urban development and the migration of the citrus industry to southern areas of the State has resulted in the conversion of many citrus groves in the area to residential land use. Undeveloped natural habitat also has been converted to residential land use. Along with changes in ground-water resource development these land-use changes have affected the water-quality characteristics of the lakes and ground water within the lake basins, particularly in reference to nitrate concentrations.

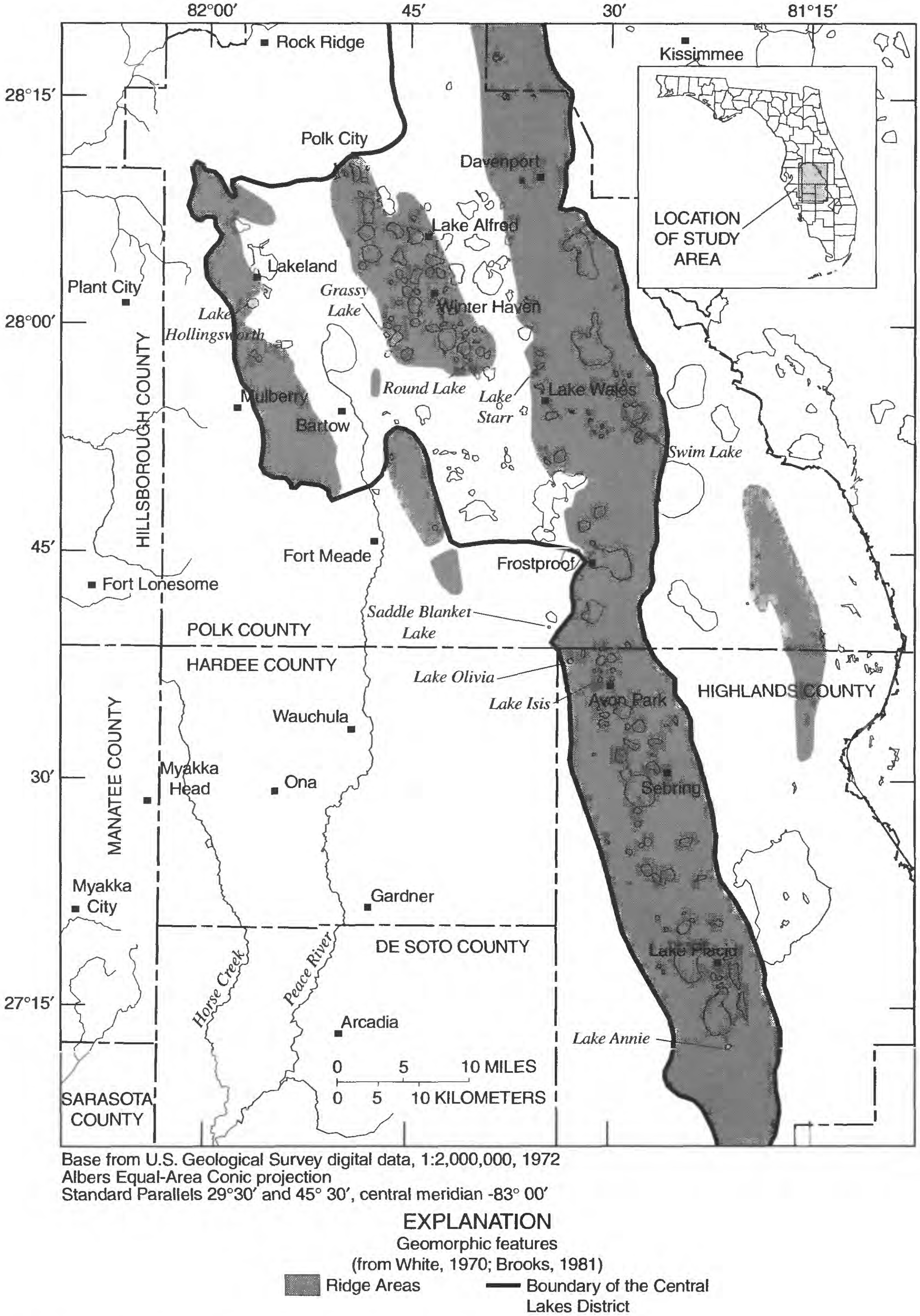


Figure 1. Locations of the lakes within the study area.

The long-term effects of elevated concentrations of nitrate on the use of local ground-water resources is of concern to residents and water-resource managers in the area. Water with elevated nitrate concentrations can be toxic to children, resulting in methemoglobinemia (blue-baby syndrome) and has been linked to increases in rates of mortality from gastric cancers (Chapelle, 1993). Nitrate concentrations greater than 10 milligrams per liter (mg/L) exceed the Florida Department of Environmental Protection's (FDEP) maximum drinking-water contaminant level. In a 1993 survey, more than 50 percent of water samples collected from domestic wells in the surficial aquifer system near Avon Park, Florida, had nitrate concentrations exceeding 10 mg/L (Florida Department of Environmental Protection, written commun., 1993). Possible sources for these high nitrate concentrations include septic-tank leachate and nitrate-based fertilizers applied to adjacent citrus groves.

Nitrate in pristine ground-water systems generally originates as naturally occurring organic nitrogen or ammonia at or near land surface, and is converted to nitrate by nitrification (Freeze and Cherry, 1979). In Florida, background ground-water nitrate concentrations are generally less than 1 mg/L (Fernald and Patton, 1984; Maddox and others, 1992; Southwest Florida Water Management District, 1996). There is no naturally existing mineral source for nitrate in Florida; therefore elevated levels of nitrate in ground water are indicative of human activity and land-use practices.

Possible anthropogenic sources of nitrate in ground water include inorganic fertilizers, animal waste associated with livestock management, human wastes from leaking sewer lines and/or septic-tank leachate, and nitrogen species found in atmospheric deposition associated with fossil fuel combustion. These sources increase the low concentrations of naturally occurring nitrate in ground water from rainwater or soil. In the study area (the Central Lakes District), land use is dominated by citrus agriculture in the ridge areas, but also includes undeveloped land, industrial/commercial land, and residential land, either with septic systems or sewer lines tied into a municipal wastewater system. Long-time fertilizer use (commonly ammonium nitrate) associated with citrus agriculture, and septic-tank leachate and leaky sewer lines associated with residential land use, are the likely sources of elevated nitrate concentrations detected in the surficial aquifer system within the study area. When nitrate-rich surface waters recharge a shallow, aerobic ground-water system, such as that commonly found within the upland ridges of the Central Lakes District, nitrate can accumulate and persist in the ground-water system, including flow paths toward discharge areas.

Nitrogen occurs as two stable isotopes: ^{15}N and ^{14}N. The ratios of these isotopes of nitrogen in nitrate (NO_3) are determined, referred to a standard, and reported as $\delta^{15}N$. Because elevated nitrate can be related to different types of human activity, numerous studies have used the $\delta^{15}N$ ratio of nitrate in ground water specifically to differentiate between organic nitrate (septic and animal waste) and inorganic nitrate (fertilizer) (Freyer and Aly, 1974; Kreitler and Jones, 1975; Kreitler, Ragone, and Katz, 1978; Gormly and Spalding, 1979; Wolterink and others, 1979; Kreitler and Browning, 1983; Flipse and Bonner, 1985; Heaton, 1986; Wells and Krothe, 1989; Aravena and others, 1993; Komor and Anderson, 1993). The $\delta^{15}N$ values fall into specific ranges for different nitrate sources including soil, fertilizers, human (sewage) and animal waste, and rainwater (fig. 2). Generally, the lighter (more negative) $\delta^{15}N$ ratios (-11 to +9 per mil) represent more inorganic nitrogen sources such as fertilizer and rainfall. Conversely, $\delta^{15}N$ values in ground water contaminated with human and animal wastes are heavier (more positive), ranging from +9 to +23 per mil. The $\delta^{15}N$ of nitrate from organic soil ranges from +2 to +9 per mil. The $\delta^{15}N$ of nitrate in rainwater ranges from -11 to +2 per mil (Heaton, 1986). Fertilizers commonly are in the range between -3 to +2 per mil (Heaton, 1986), although values as light as -8 per mil have been reported. A compilation of $\delta^{15}N$ data from various sources by Rolston and others (1994) also illustrates the trend of heavier signatures associated with organic nitrate sources. Nitrogen-isotope data for ground water in Florida have been shown to be within these published ranges of -11 to +23 per mil (Wolterink and others, 1979; Berndt, 1990; Trommer, 1992; Jones and Upchurch, 1993; Andrews, 1994; Hornsby, 1994; Jones and others, 1994; Jones and Upchurch, 1996).

Purpose and Scope

In 1995, the U.S. Geological Survey (USGS), in cooperation with the Florida Department of Environmental Protection, began a 2-year study to evaluate the nitrogen-isotope technique for identifying sources of nitrate in ground water in the Central Lakes District of

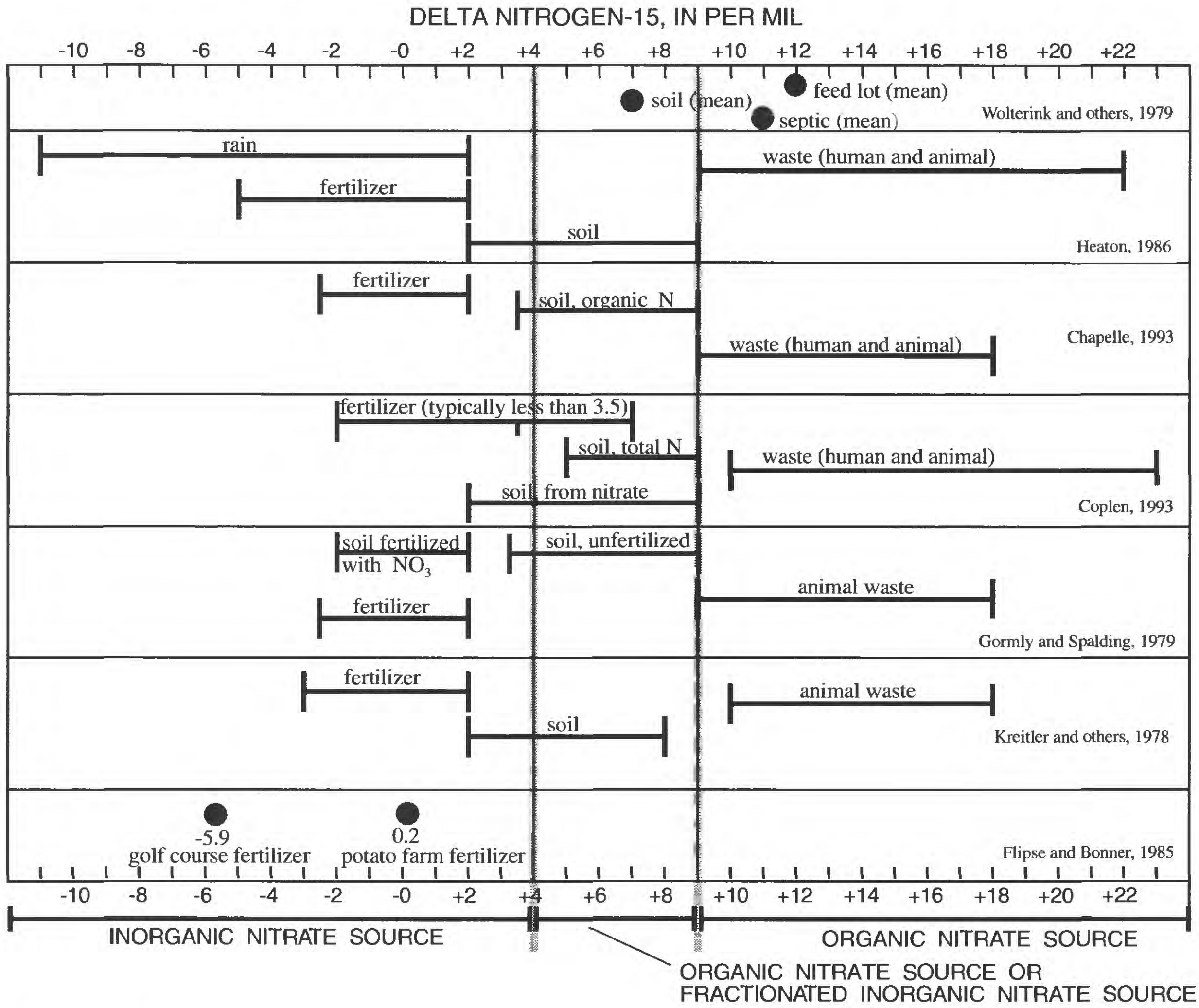


Figure 2. Published ranges of nitrogen-isotope signatures ($\delta^{15}N$) for various sources of ground-water nitrate.

Florida. Ten lakes within the Central Lakes District of Florida are part of an ongoing USGS water-budget investigation. This nitrogen-isotope study complements the water-budget investigation and provides additional data that can be used to better understand the land use, ground-water chemistry, and water budgets for those lakes. This report presents the results from those evaluations of the surficial aquifer system in nine lake basins in the Central Lakes District, in Polk and Highlands Counties. Each basin was selected for nitrogen-isotope sampling to represent specific dominant land-use types (undeveloped, citrus, residential, and mixed) and on the basis of previously sampled high nitrate concentrations in the ground water. Six of the nine lake basins are in Polk County: Lake Hollingsworth, Grassy Lake, Lake Starr, Swim Lake, Round Lake, and Saddle Blanket Lake. The remaining lake basins are in Highlands County: Lake Isis, Lake Olivia, and Lake Annie. A total of 36 wells and two lakes (Isis and Swim) were sampled twice during 1996. Lake and ground-water samples from the nine lake basins were collected and analyzed for nitrogen isotopes, nitrate, and selected other water-quality constituents. The water-quality data are presented in this report and the relation between the sources and concentrations of nitrate in the study area is discussed. Field and analytical methods are described in the Methods and Approach section.

Description of Study Area

The Central Lakes District is a mantled karst region, where surficial deposits of unconsolidated sands and clays overlie a buried, irregular limestone surface. The sands and clays have settled into the limestone surface as a result of subsidence activity associated with limestone dissolution and subsequent infilling of solution features. Sinkholes and depression features are prevalent throughout the region and are often occupied by water, thus forming lakes. The lakes may be internally drained or connected to surface flow depending on the local geologic structure, man-made features, hydraulic gradients, and topography. Water-budget investigations of these lakes indicate that lake levels fluctuate primarily in response to precipitation, ground-water inflow, and leakance. More than 70 percent of the approximately 7,800 Florida lakes over 1 acre in size, are classified as seepage lakes, having no surface water inflow or outflow (Brenner and others, 1990). Previous reports by Sinclair and others (1985), Barcelo and others (1990), Lee and others (1991), and Tihansky and others (1996) describe the hydrogeology and sublake geologic structure within the Central Lakes District. A typical schematic illustrating the hydrogeologic framework beneath a seepage lake within the district is shown in figure 3. When a downward head gradient exists, the discontinuity of the clay units and the reworking of surficial deposits into buried solution features beneath these lakes create a preferential avenue for downward ground-water movement from the surficial aquifer system into the Upper Floridan aquifer.

The surficial aquifer system and the Upper Floridan aquifer are used for public and private drinking-water supplies in the study area. Because of the permeable nature of the surficial sands in the area, the potential for nitrate and other contaminants to be transported from the land surface to the shallow ground-water system exists. The presence of elevated concentrations of nitrate in the surficial aquifer system in the study area demonstrates the vulnerability of the surficial aquifer system to contamination. The transport of nitrate into the shallow ground-water system can degrade not only surface waters (such as lakes), and shallow drinking water supplies, but also deeper ground-water supplies as ground water migrates from the surficial aquifer system into the underlying Upper Floridan aquifer by way of sinkholes, subsidence features, and head gradients.

Within the study area, the surficial aquifer system ranges from 50 to 300 feet (ft) in thickness and is composed of unconsolidated sand and clay. The surficial aquifer system is hydrologically separated from the underlying Upper Floridan aquifer by the intermediate confining unit (fig. 3), although sinkholes and subsidence features often modify and breach the confining unit, thereby diminishing the hydrologic confinement. The intermediate confining unit is thin and discontinuous to the north and east and thickens to the south and west, where it is part of the intermediate

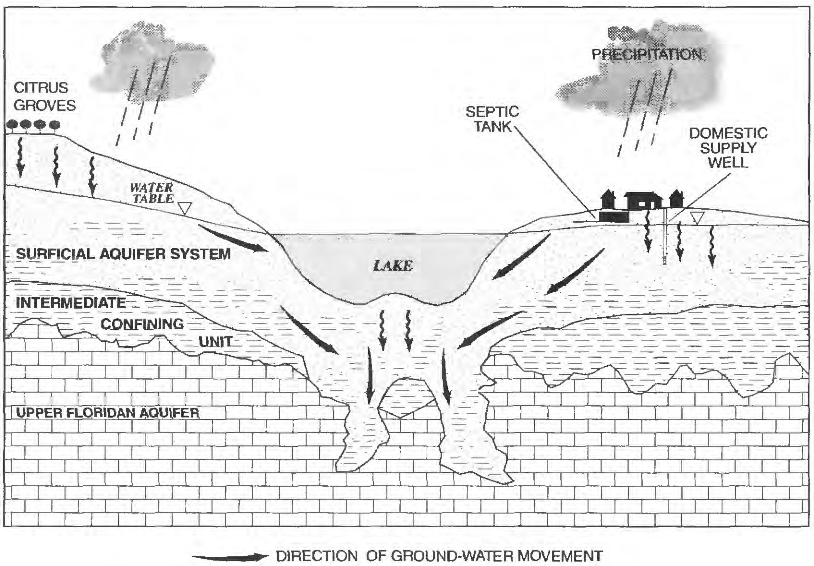


Figure 3. Generalized hydrogeologic framework beneath a lake within the Central Lakes District, Florida.

aquifer system. The intermediate aquifer system varies both in lithology and thickness within Polk and Highlands Counties. Beneath the intermediate confining unit/intermediate aquifer system, are the carbonates of the Upper Floridan aquifer. The top of this hydrogeologic unit occurs from 200 ft below land surface in the northern part of the study area to 600 ft below land surface in the southern part of Highlands County (Tihansky and others, 1996).

The surficial aquifer system and lakes within pristine basins in the study area are characterized by dilute water with relatively low pH and high dissolved oxygen concentrations (Brezonik and others, 1983; Canfield, 1983; Brenner and others, 1990; and Stauffer and Canfield, 1992). The high recharge rates and poorly developed soils allow for rapid percolation of rainwater through the clean sands of the surficial aquifer system, resulting in only a slight addition of dissolved species in pristine areas. However, various land-use practices can result in solute loading from land surface to the surficial aquifer system.

Acknowledgments

The authors thank the Nature Conservancy, Archbold Biological Station, and private land owners within these lake basins for access to their property and for permitting the USGS to install, monitor, and sample ground-water wells. Thanks also to Dr. Ashok Alva of the University of Florida Citrus Research Center for his useful information regarding citrus fertilizer chemistry and applications. The authors also thank Dr. Johnkarl Bohlke of the U.S. Geological Survey for supplying $\delta^{15}N$ standards to the University of Florida Wetlands Soils Research Laboratory and for assisting in the calibration and interpretation of the $\delta^{15}N$ isotope data.

METHODS AND APPROACH

Field and analytical methods used during this study are described below. A summary of land use for each lake basin and the application of nitrogen-isotope techniques used to identify nitrate sources are also discussed.

Site Selection

Ten lakes, within different land-use areas in Polk and Highlands Counties, are part of an ongoing USGS water-budget investigation. As part of the water-budget investigation, a network of surficial aquifer system monitoring wells was installed and ground water was sampled for major ions and nutrients within each of the lake basins. This sampling provided background data for the water-quality characteristics as well as the ground-water flow paths within each lake basin. Nine of the 10 lakes were selected for the nitrogen-isotope study because of the known land use within each basin and the likely sources of nitrate to the ground water.

Seven of the nine selected lake basins are considered representative of typical seepage lake basins. Lake Annie and Lake Hollingsworth are not considered seepage lakes because they have surface-water outflow.

Each lake basin was classified as having one of four predominant land-use types: (1) undeveloped, representing background conditions; (2) residential, with sewer and septic tanks; (3) citrus agriculture; and (4) mixed, which includes the three types mentioned above as well as some commercial/industrial land use. Two lake basins in the study area, Lake Annie basin in Highlands County and the basin of the larger of two lakes known as the Saddle Blanket Lakes in Polk County, are within undeveloped or preserved highlands scrub habitat. Although the Saddle Blanket Lake basin is in an upland area, it is not actually within the Central Lakes District, but was selected to represent an undeveloped lake basin within an upland area where the effects of human activity have been minimal. The Lake Hollingsworth basin (the majority of homes are tied into a municipal sanitary sewer system) in Polk County and the Lake Olivia basin (homes that have individual septic waste-disposal systems) in Highlands County were selected to represent two types of residential land use. The basins of Swim Lake (name used by local residents, no formal name designated) and Round Lake, both in Polk County, contain predominantly citrus land use. The basins of Lake Starr, Grassy Lake, and Lake Isis were selected to represent mixed land use.

Monitoring wells within each lake basin were selected for sampling on the basis of ground-water flow direction and previously determined nitrate concentrations in the surficial aquifer system. The selected monitoring wells also were in ground-water recharge areas so that land-use effects could be observed. The wells selected for sampling were (1) within or downgradient from representative land-use types, (2) generally upgradient from the lake, and (3) along a representative ground-water flow path to the lake. Two sample collection periods in 1996 corresponded to the seasonal wet (fall) and dry (spring) hydrologic conditions. The wet season is associated with higher recharge from rainfall, whereas the dry season is associated with lower recharge and a period of time when inorganic-nitrogen based fertilizer is commonly applied to citrus groves.

Field Methods

Water samples from 36 wells and two lakes were collected during April-May 1996 and October-November 1996. The monitoring wells consisted of 2-inch polyvinylchloride (PVC) casing tapping the top of the saturated zone of the surficial aquifer system. Each well was finished 5 to 10 ft below the water table and had a 5-ft screened interval. The wells were named using letters to describe their location based on whether they were in the upper part (U) or lower part (L) of the lake basin followed by their directional orientation around the lake. For example, the lower northwest well is named LNW.

Each well was purged prior to sample collection. A peristaltic pump was used to remove at least three casing volumes of water from the well. In some wells, the depth to water exceeded the lift capacity of the peristaltic pump and the three volumes of water were removed using a Teflon bailer. The field measurements were made from sample water collected at the pump or bailer. The water samples were analyzed in the field for temperature, pH, specific conductance, and dissolved oxygen.

Dissolved oxygen was measured in a closed flow-through cell to eliminate aeration. In wells that were bailed, a dissolved oxygen probe was lowered into the well, and dissolved oxygen was measured directly in the well. In some cases, the depth to water exceeded the cable length of the dissolved oxygen probe, so dissolved oxygen concentrations could not be measured. For this study, dissolved oxygen concentrations less than 1.5 mg/L are considered indicative of anaerobic or near anaerobic conditions where denitrification reactions can occur. In this report, dissolved oxygen concentrations are reported with a detection limit of 0.5 mg/L.

After field determinations stabilized, samples were collected for laboratory analysis. Nutrient species and $\delta^{15}N$ ratio determinations were made in the laboratory. For samples with low nitrate concentrations, larger volumes of sample water were collected for the $\delta^{15}N$ ratio determinations. Nitrate concentrations included in this report are nitrate-N concentrations and are reported with nitrite, ammonia, and organic nitrogen concentrations in the appendix.

Analytical Methods

The $\delta^{15}N$ ratios of nitrate in the water samples collected during this study were determined by mass spectrometer using the analytical method of Burke and others (1990). All samples were prepared on zeolite and run in duplicate. The mean concentrations of the duplicate analyses are presented in the appendix. Potassium nitrate (KNO_3) standards were analyzed for $^{15}N/^{14}N$ with each sample set. Fractionation was determined to occur as a result of sample preparation; therefore, additional standards for N-isotopic abundance were submitted to the University of Florida Wetlands Soil Research Laboratory (UFWSRL) for analysis. These KNO_3 standards were used to correct the final analytical data for fractionation effects before interpretations were made.

Although the Burke and others (1990) method is not used for natural abundance determinations, the precision associated with this method was sufficient to differentiate between organic and inorganic sources of nitrogen. The difference from the mean was computed for each sample. The average difference was +/- 0.9 per mil, which is an indicator of analytical precision for this data set. Where nitrate concentrations were below detection limits, greater sample volumes were collected to obtain sufficient nitrate concentrations for isotope analysis.

Application of Nitrogen-Isotope Analytical Determinations

Nitrogen occurs as two stable isotopes: ^{15}N and ^{14}N. Distinguishing whether nitrogen in ground water originated from agricultural fertilizers (inorganic nitrogen) or sewage effluents (organic nitrogen) is done by determining the natural abundance of these isotopes present in nitrate. By measuring the natural abundance of the ratios of these nitrogen isotopes ($^{15}N/^{14}N$) in ground-water nitrate, distinct isotopic signatures can be used to identify the source of the nitrate. Ratios of these isotopes are often compared to a standard, calculated and reported as $\delta^{15}N$ as shown here (Letolle, 1980):

$$\delta^{15}N \text{ in per mil} = [(^{15}N/^{14}N)\text{ sample }/(^{15}N/^{14}N)\text{ standard } - 1] \times 1{,}000. \quad (1)$$

Sources of nitrate in the study area include: atmospheric deposition, soil, fertilizer, and human and animal wastes. Ranges of $\delta^{15}N$ for nitrate from different sources are shown in figure 2. The concentrations of nitrogen species in rainwater are generally less than 1.0 mg/L (Irwin and Kirkland, 1980; Brezonik and others, 1983; Baker, 1991; Pollman and Canfield, 1991). Nitrogen species in dry deposition in the ridge area have been found to less than (87 percent) of inputs from wet deposition (Baker, 1991). The young, nutrient-deficient, sandy soils (entisols-quartzipsamments) characteristic of the ridge area do not contain significant amounts of nitrogen-rich organic matter (Brown and others, 1990). Although nitrogen in atmospheric deposition can be a significant source of nitrate in ground water, especially in undeveloped land-use areas, it is an unlikely source for elevated levels of nitrate in ground water in the study area because of the low concentrations relative to those found in ground water and nitrate from other sources. The most likely sources within the study area are fertilizers and human and animal wastes (Maddox and others, 1992). Based on published ranges for $\delta^{15}N$ (fig. 2), there is a significant difference between the $\delta^{15}N$ signature of fertilizers (-6 to +7 per mil) and the $\delta^{15}N$ signature of human and animal waste (+9 to +22 per mil). These differences make this technique useful and applicable to this study area.

Although the $\delta^{15}N$ signature of nitrate in ground-water samples can directly reflect the original source of the nitrate, other factors can affect the $\delta^{15}N$ signature. Nitrate accumulates in ground water under oxygenated conditions (nitrification) and is converted to reduced species of nitrogen under anaerobic conditions (denitrification). The extent and type of microbially-mediated nitrogen cycling reactions can determine which nitrogen species are present in ground water. Loss of nitrate by denitrification requires four conditions to occur: (1) the presence of nitrogen oxides as terminal electron acceptors, (2) the presence of bacteria possessing the metabolic capacity, (3) suitable electron donors, such as organic carbon and iron, and (4) anaerobic conditions or restricted availability of dissolved oxygen (Firestone, 1982 and Korom, 1992). Under aerobic conditions, oxidation of organic nitrogen (nitrification) compounds can occur:

$$\text{organic-N} \dashrightarrow NH_4^+ \dashrightarrow NO_2^- \dashrightarrow NO_3^- \text{ (nitrification).} \quad (2)$$

Under anaerobic conditions, denitrification reactions can occur, converting nitrate to nitrite and ultimately to nitrogen gas:

$$NO_3^- \dashrightarrow NO_2^- \dashrightarrow NO \dashrightarrow N_2O \dashrightarrow N_{2\,(g)} \text{ (denitrification).} \quad (3)$$

Fractionation of the two nitrogen isotopes occurs during these reactions because the lighter ^{14}N is preferentially used in biological reactions, resulting in residual ground-water nitrate enrichment with ^{15}N. These fractionation reactions are described in more detail by Letolle (1980), Bottcher and others (1990), and Herbel and Spalding (1993). The ammonia component of a commonly applied form of citrus fertilizer (ammonium nitrate) can be converted to nitrate and also enrich the ground water in the heavier ^{15}N. However, both volatilization and denitrification reactions of an inorganic nitrogen source do not appear to increase $\delta^{15}N$ of nitrate above +10 per mil (Flipse and Bonner, 1985; Chapelle, 1993). Thus, the nitrogen isotopes can be used to distinguish between inorganic (fertilizers) and organic (human and animal waste) sources of nitrate.

EVALUATION OF NITRATE SOURCES IN DIFFERENT LAND-USE AREAS BASED ON NITROGEN-ISOTOPE SIGNATURES

Nitrogen-isotope ratios determined during this study are related to the different land-use types identified within the Central Lakes District. Within the undeveloped, residential, citrus, and mixed land-use areas, the relation between the nitrogen-isotope signatures, nitrate concentrations, dissolved oxygen concentrations ground-water flow patterns, and land use is discussed.

Undeveloped Lake Basins

Two lake basins, Annie and Saddle Blanket (figs. 4 and 5), were selected to represent background concentrations of nitrate in the ground water from natural settings within the Central Lakes District. Lake Annie is at the southern edge of the Lake Wales Ridge and within the Archbold Biological Station, a large nature preserve. The other lake, Saddle Blanket Lake, is in another land preserve managed by the Nature Conservancy in Polk County. Both lake basins do not contain any agriculture, industry, or domestic residential activities, although both properties are surrounded by citrus agriculture. Nitrate concentrations and $\delta^{15}N$ signatures from ground water in these two lake basins, therefore, probably represent background levels of nitrate that are unaffected by human influences.

Nitrate concentrations in ground water beneath the well-drained, poorly developed soils of the natural scrub areas are expected to be low. Any nitrate in the soils of these oligotrophic communities generally is taken up by vegetation or by the microbial community. Likely sources of nitrate in these natural areas are usually atmospheric deposition and organic matter in soils. Typical ranges of the $\delta^{15}N$ signatures of nitrate from these two sources are shown in figure 2. If denitrification reactions occur, microbial fractionation of these nitrate sources could alter the organic soil $\delta^{15}N$ value to higher values (greater than +10 per mil), resembling signatures from organic (human and animal) waste sources.

Although Lake Annie is surrounded by undeveloped land, citrus agriculture and industrial/commercial activities are present near the upper parts of the ground-water basin to the north, west, and northeast (fig. 4a). Ground-water inflow to Lake Annie occurs in the area near wells LW and LS, which were both sampled for nitrogen isotopes. Nitrate concentrations in the surficial aquifer system were below detection limits of 0.002 mg/L, and the $\delta^{15}N$ of nitrate ranged from +9.7 to +16.6 per mil (fig. 4b). The low nitrate concentrations suggest that all available nitrate has been used by vegetation or converted by microbial activity, either by assimilatory or dissimilatory nitrate reduction. The heavier $\delta^{15}N$ ratio signatures suggest that the minimal amount of nitrate present in the ground water is primarily of organic origin. Soil-derived nitrate most likely would be the source of nitrate in this undeveloped

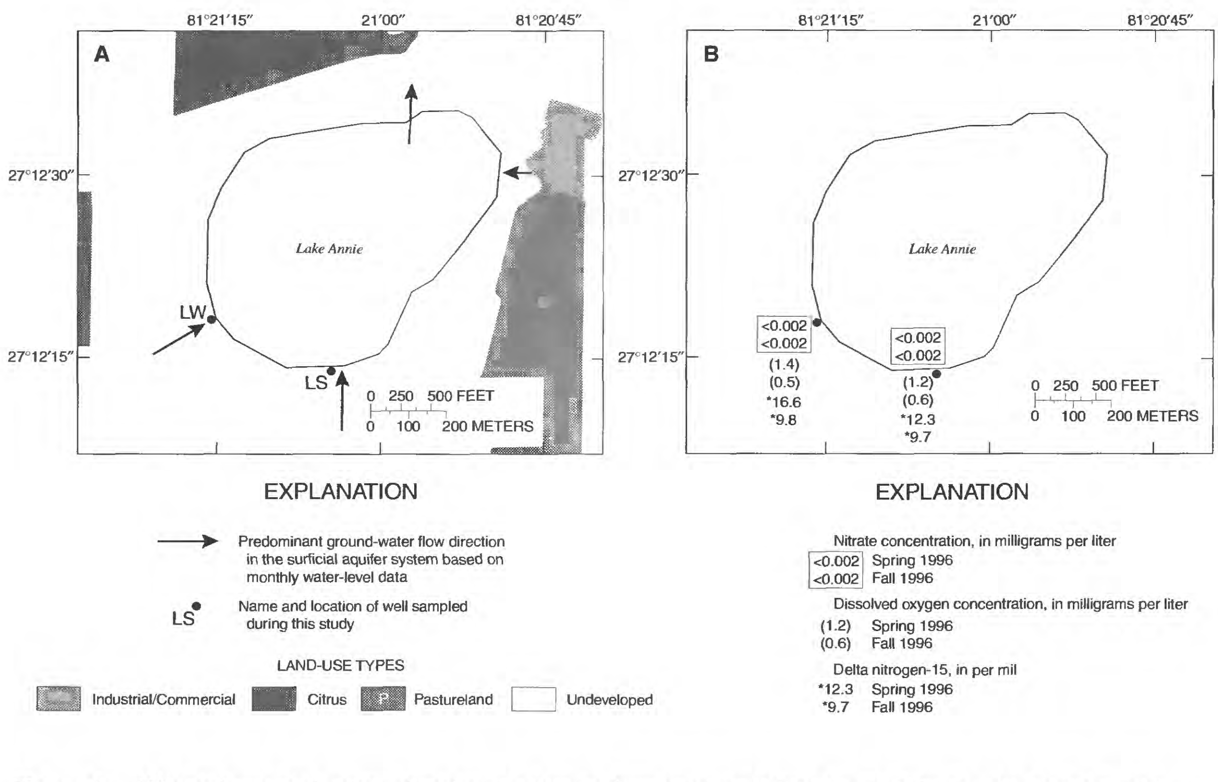


Figure 4. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Lake Annie basin, Highlands County, Florida.

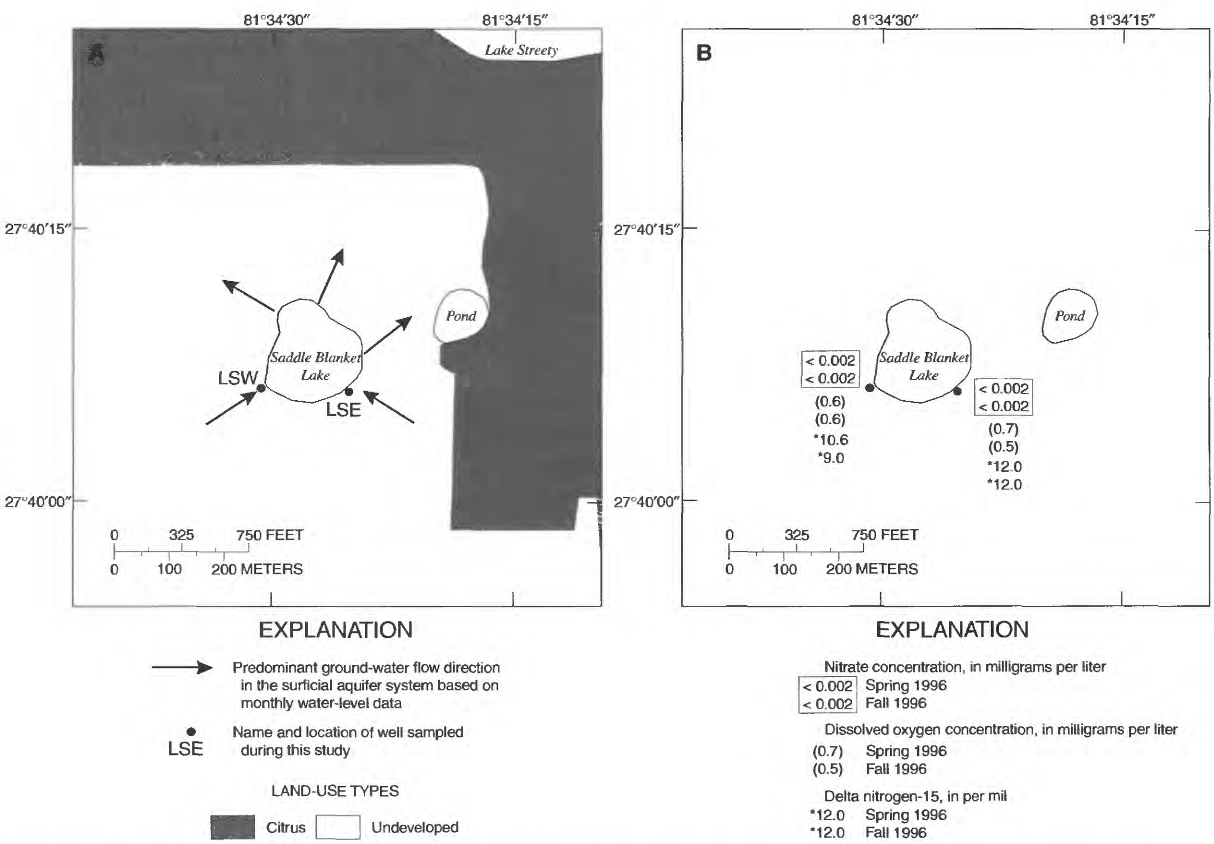


Figure 5. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Saddle Blanket Lake basin, Polk County, Florida.

land-use area. Organic soil nitrogen, further fractionated by microbial reactions, has resulted in a heavier (more positive) signature in the ground water. Indirect evidence of these microbial reactions is suggested by the dissolved oxygen concentrations in the surficial aquifer system at Lake Annie. The dissolved oxygen concentrations in the two wells sampled during this study ranged from 0.5 to 1.4 mg/L. Both the lack of high nitrate concentrations and the relatively low dissolved oxygen values indicate that the system is close to being anaerobic, and the reduction of nitrate by microorganisms can occur. Because of the low concentration of nitrate, there can be greater uncertainty associated with these samples because there is less nitrogen to analyze. However, there did not appear to be any relation between the precision of the analyses and the nitrate concentrations.

Saddle Blanket Lake is located on undeveloped property adjacent to citrus agricultural areas. The predominant land use north and east of Saddle Blanket Lake is citrus agriculture (fig. 5a). Ground-water inflow to the lake occurs in areas near both the LSW and the LSE wells. Nitrate concentrations in water samples obtained from these wells were below the detection limit of 0.002 mg/L. The $\delta^{15}N$ values ranged from +9.0 to +12.0 per mil (fig. 5b). Dissolved oxygen concentrations were close to detection limits (0.5 to 0.7 mg/L). These conditions suggest that denitrification reactions likely occur within this lake basin. The heavier $\delta^{15}N$ signatures, although susceptible to uncertainty because of the low nitrate concentrations, suggest that microbial fractionation of organic source nitrogen can occur.

Lake Annie and Saddle Blanket Lake, located in similar environmental settings, had similar nitrate concentrations and $\delta^{15}N$ signatures. Generally, data collected from these lake basins indicate that little nitrate is available to enter the ground-water system, and if any nitrate is present, it is probably utilized by the anaerobic, nitrate reducing microbial communities within the soil zone and surficial aquifer system. Controlled burning, which is part of the management of these undeveloped lake basins, probably contributes the initial carbon to the surficial aquifer system, thereby lowering dissolved oxygen concentrations.

Concentrations of dissolved organic carbon determined for several ground-water samples collected in these basins have been as high as 40 mg/L. Because the system is not limited by low carbon, the efficient depletion of oxygen results in anaerobic ground water where denitrification reactions might occur.

Residential Land-Use Lake Basins

Lake Hollingsworth and Lake Olivia (figs. 6 and 7) both represent lake basins in residential land-use areas (figs. 6a and 7a); however, these two residential settings differ significantly. At Lake Olivia, single family homes were built on property that was previously natural scrub habitat with no likely source of ground-water nitrate. Much of the surrounding properties are either undeveloped scrub habitat or citrus agriculture. There is no municipal water supply or wastewater system; therefore all of these homes rely on ground water for water supply and septic systems for wastewater disposal.

In contrast, the Lake Hollingsworth basin has been affected by various types of land use since the late 1800's including citrus groves, regional phosphate mining activity, road building and runoff, recreational facilities, and residential properties. Current land use is dominated by residential properties; however, Florida Southern College is located along the northern shore and a private country club is located along the southwestern shore. Both of these facilities have landscaping maintenance programs. Historically, the residential homes surrounding Lake Hollingsworth used ground water for their domestic water supply and septic systems for domestic wastewater disposal. However, between 1929 and 1965, nearly all wastewater systems within the lake basin were connected to sewer lines maintained by the City of Lakeland. There are many sources of nitrate in the ground water as a result of the varied land use over time. Aside from fertilizer associated with landscaping or from the few remaining septic tanks or leaking sewer lines, contributions of nitrate to the ground-water system associated with current land use should be minimal.

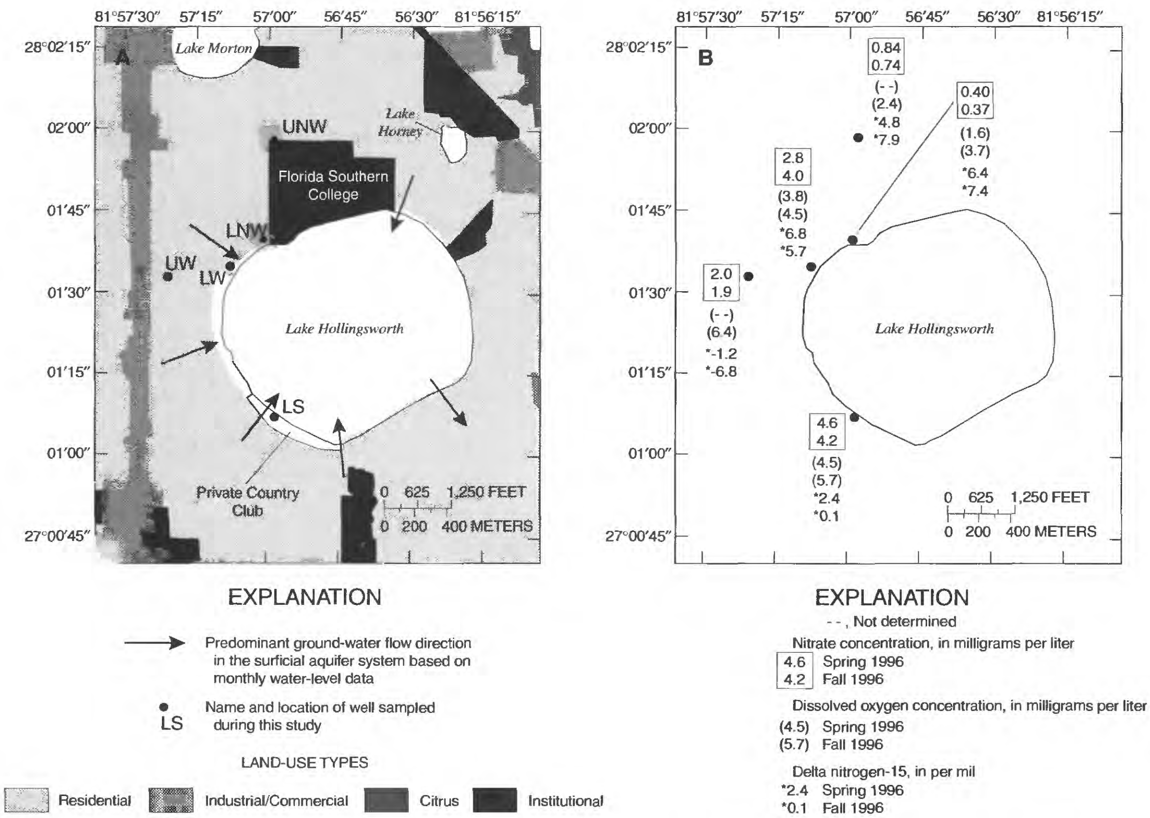


Figure 6. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Lake Hollingsworth basin, Polk County, Florida.

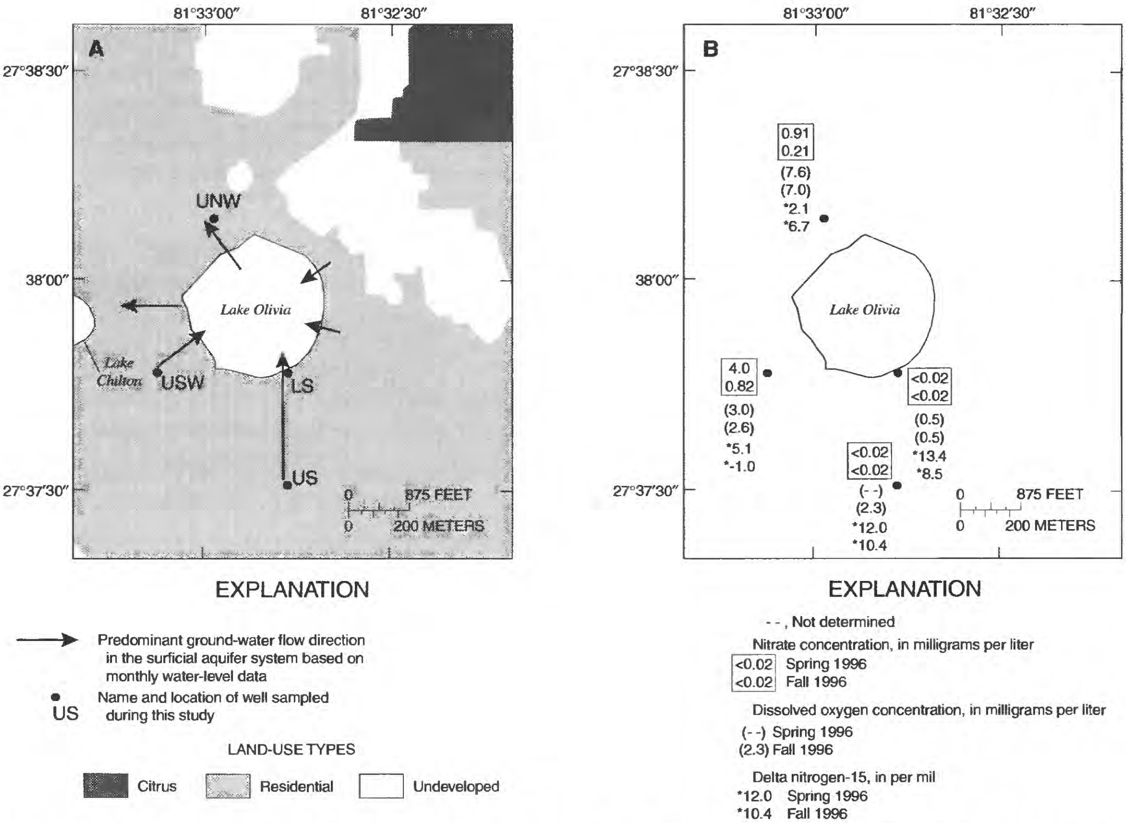


Figure 7. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Lake Olivia basin, Highlands County, Florida.

Ground-water inflow to Lake Hollingsworth occurs along flow paths near wells LS, UNW, LNW, UW, and LW (fig. 6a). Nitrate concentrations from these wells ranged from 0.37 to 4.6 mg/L (fig. 6b). The $\delta^{15}N$ values ranged from -6.8 to +7.9 per mil. These values indicate that inorganic nitrogen is probably the dominant source of ground-water nitrate. Dissolved oxygen concentrations ranged from 1.6 to 6.4 mg/L. The highest nitrate concentrations corresponded to the lightest $\delta^{15}N$ values, which also corresponded to ground water with higher dissolved oxygen concentrations. These values and concentrations indicate an inorganic fertilizer source of detected nitrate within conditions that are unfavorable for removing nitrate from the ground water.

Ground-water inflow to Lake Olivia occurs along flow paths near wells UNW, USW, LS, and US (fig. 7a). Nitrate concentrations in these wells ranged from below the detection limit of 0.02 mg/L, similar to ground water in the undeveloped land-use areas, to 4.0 mg/L (fig. 7b). The $\delta^{15}N$ values in ground water ranged from -1.0 to +13.4 per mil, indicating that inorganic and organic sources of ground-water nitrate are likely present. The heavier $\delta^{15}N$ values correspond to the lowest nitrate concentrations and probably reflect microbial fractionation of an organic nitrogen source. This source could be a natural soil source, similar to that observed at Lake Annie and Saddle Blanket Lake, or could be from septic-tank leachate. However, the low nitrate concentrations indicate that little nitrate from septic systems is entering the ground-water system. Although the nitrate concentration is below the detection limit of 0.02 mg/L at both the LS and the US wells, the dissolved oxygen concentration at the US well is 2.3 mg/L and downgradient at the LS well it is less than 0.5 mg/L (anaerobic). Denitrification fractionation could be occurring as redox conditions in ground water change from aerobic to anaerobic conditions. In the areas where wells USW and UNW are located, the dissolved oxygen levels are near 3 and 7 mg/L, respectively, and nitrate concentrations are higher, ranging from 0.21 to 4.0 mg/L. The $\delta^{15}N$ data values suggest the influence of an inorganic source of nitrate that could be of greater significance than an organic source, although these $\delta^{15}N$ signatures fluctuate between spring and fall. This fluctuation could reflect differences in seasonal recharge events, residential fertilizer applications, or the effect of seasonal occupation of local residences and associated fluctuations in septic-system usage. The significant concentrations of dissolved oxygen also contribute to the accumulation of nitrate observed at both sites. Citrus groves are present to the north of Lake Olivia. Although they do not appear to be within the drainage basin of the lake, fertilizer associated with citrus agriculture could reach the Lake Olivia basin by runoff, ammonia aerosols, or ground-water flow through sinkhole or depression features. Volume weighted mean values of nitrate and ammonia from rain samples collected in the Central Lakes District were 0.62 mg/L and 0.10 mg/L, respectively (Pollman and Canfield, 1991).

Within the residential settings surrounding Lake Hollingsworth and Lake Olivia, nitrogen isotope data indicate that the dominant ground-water nitrate source is of inorganic origin. Fertilizer use by homeowners and landscaping maintenance may be increasing the ground-water nitrate concentrations. In areas where organic sources are indicated by heavier nitrogen-isotope ratios, the nitrate levels are not elevated above the 0.02-mg/L detection limit. The $\delta^{15}N$ signatures become heavier during downgradient movement of these waters, suggesting that some microbial fractionation by denitrification occurs. The aerobic state of the ground water is of major importance. The presence of dissolved oxygen prevents denitrification reactions, thus allowing nitrate to accumulate in greater concentrations.

Citrus Land-Use Lake Basins

The basins of Round Lake and Swim Lake (figs. 8 and 9) are located in citrus agricultural land-use areas. The surface area of both lakes is small (less than 30 acres) and their drainage basins are located entirely within active citrus groves. A residential area lies west of the Round Lake ground-water basin (fig. 8a), and should not affect the water quality within the Round Lake basin.

Ground-water inflow to Round Lake occurs along flow paths near wells UN, LN, USE, and LSE (fig 8a). Nitrate concentrations in ground water from

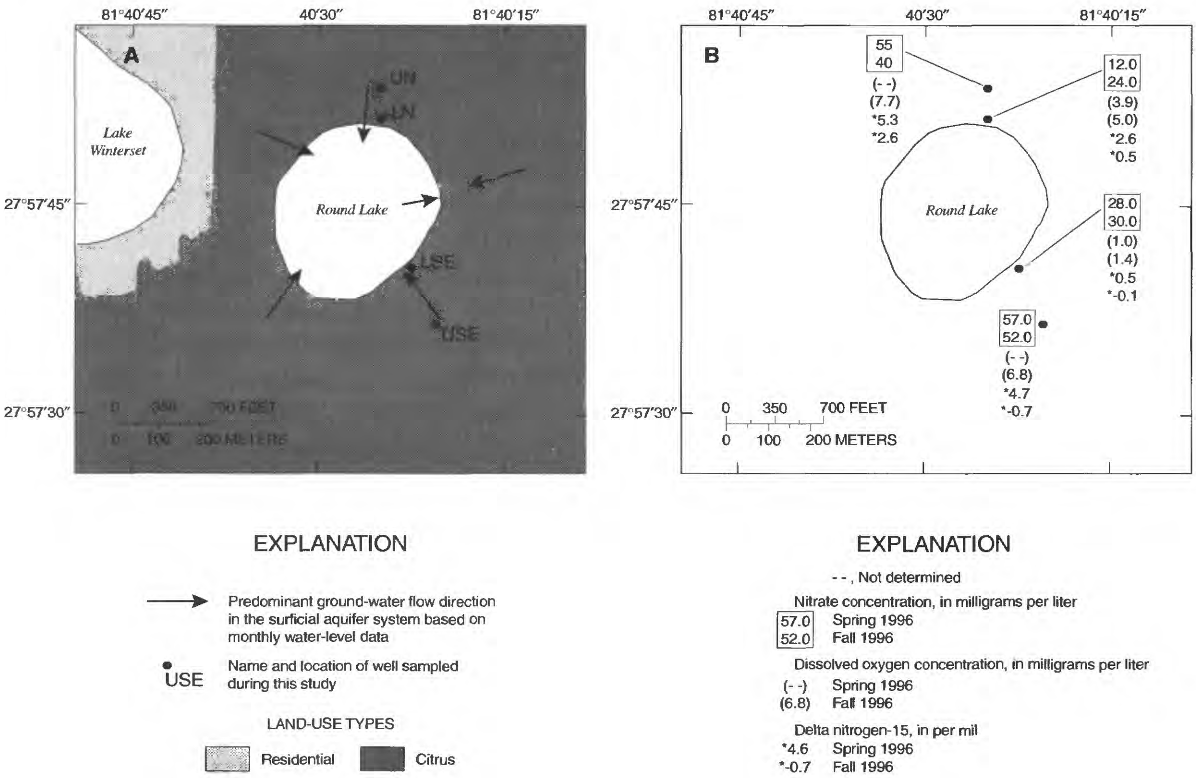


Figure 8. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Round Lake basin, Polk County, Florida.

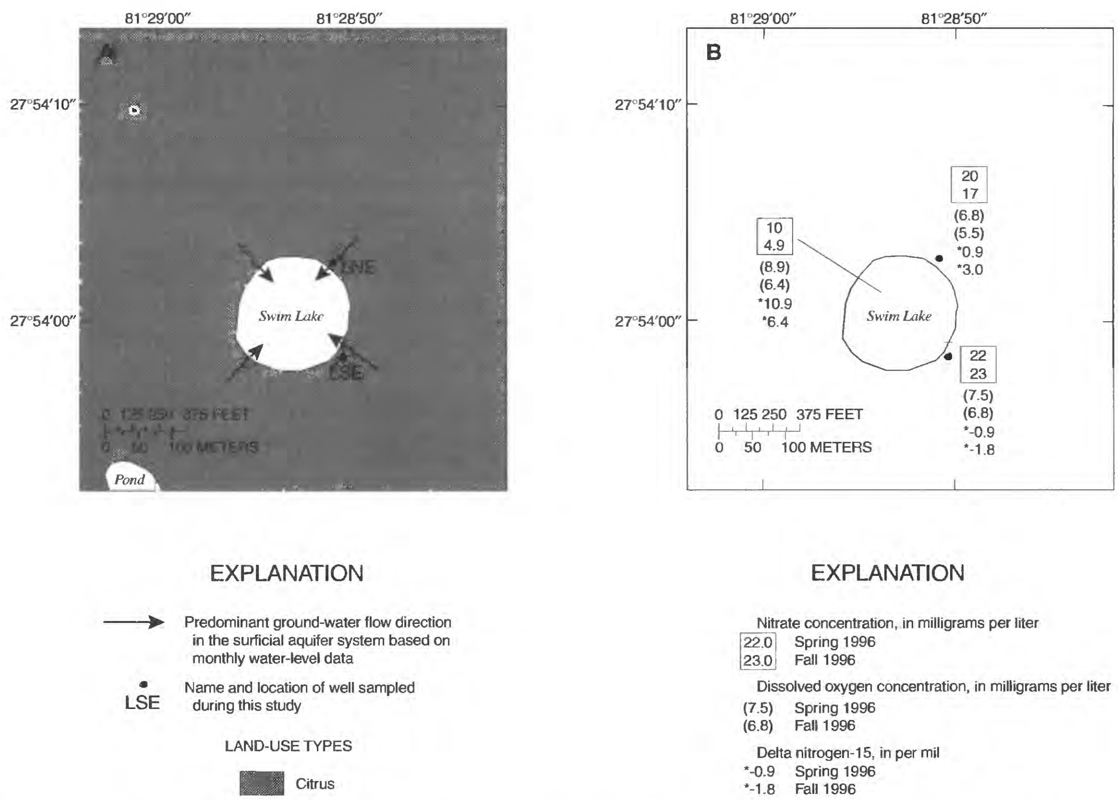


Figure 9. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Swim Lake basin, Polk County, Florida.

these wells ranged from 12 to 57 mg/L (fig. 8b). The $\delta^{15}N$ signatures of ground-water samples ranged from -0.7 to +5.3 per mil.

Ground-water inflow to Swim Lake occurs along flow paths near wells LNE and LSE (fig. 9a). Nitrate concentrations in ground water from these wells ranged from 17 to 23 mg/L (fig. 9b). The $\delta^{15}N$ signatures of ground-water samples ranged from -1.8 to +3.0 per mil (fig. 9b).

The $\delta^{15}N$ signatures indicate an inorganic source of ground-water nitrate within both lake basins. These values correspond to the ranges for a fertilizer source (fig. 2). These basins have been used for citrus cultivation for more than 30 years, and continual seasonal applications of inorganic-N fertilizer to the sandy soils rapidly migrate into the surficial aquifer system. Dissolved oxygen concentrations in the surficial aquifer system at Round Lake ranged from 1.0 to 7.7 mg/L (fig. 8b); in the surficial aquifer system at Swim Lake, they ranged from 5.5 to 7.5 mg/L (fig. 9b). The poorly developed soils with low organic content, together with aerobic ground-water, create conditions that favor nitrification reactions. The high dissolved oxygen concentrations prevent denitrification or the microbial removal or conversion of any excess nitrate associated with fertilizer applications. As a result, nitrate has accumulated in the ground water and occurs at levels that exceed the FDEP maximum allowable concentrations for drinking water standards (10 mg/L).

The $\delta^{15}N$ values for surface-water samples collected at Swim Lake were +6.4 and +10.9 per mil (fig. 9b). This lake had significant measured nitrate concentrations (4.9 and 10.0 mg/L). If nitrogen cycling in the surface-water system of Swim Lake occurs, this biological activity would fractionate any nitrate derived from ground-water inflow as it is incorporated into microbial and other biological pathways. This fractionation would result in the lake having $\delta^{15}N$ signatures that are heavier than those for the ground water. Although these lake $\delta^{15}N$ signatures are slightly heavier than those of the ground water, they do not exceed +10 per mil, and therefore indicate an inorganic source of nitrate (fig. 2).

Mixed Land-Use Lake Basins

Three lake basins were selected to best represent the ground-water characteristics of lake basins with mixed land use. Land use at Grassy Lake, Lake Isis, and Lake Starr includes residential septic and sewer, citrus agriculture, and some industrial/commercial activities (figs. 10, 11, and 12).

Grassy Lake is surrounded by approximately 50 percent citrus agriculture extending to the lake shoreline (fig. 10a). The residential properties use individual septic systems for wastewater disposal, and many of the properties are located along the lake shoreline. Several of the houses along the shoreline were built at a time when the lake stage was lower and, consequently, are below flood level. As a result of flooding conditions in 1995 and 1996, several of these homes have been abandoned, and a few septic tanks are probably a part of the lake bottom.

Ground-water inflow to Grassy Lake occurs along flow paths near wells LS, LE, and LNE (fig. 10a). Nitrate concentrations in water from these wells ranged from 0.12 to 37.0 mg/L (fig. 10b). Highest nitrate concentrations were observed in water from wells downgradient from citrus groves. The nitrogen-isotope ratios in ground water from these sites ranged from +0.3 to +13.0 per mil. At the LS and LNE wells, which are downgradient from citrus land use, the $\delta^{15}N$ values clearly indicate an inorganic source (+0.3 to +7.3 per mil). However, at the LE well, which is within a residential area, nitrate concentrations are lower and the $\delta^{15}N$ values (+10.9 and +13.0 per mil) indicate an organic nitrate source.

At most of the Grassy Lake wells, the dissolved oxygen levels were close to the detection limit of 0.5 mg/L and some anaerobic microbial activity probably occurred. At the LNE well, results of the spring and fall samplings reflect the sensitivity of nitrate to dissolved oxygen levels. Although neither $\delta^{15}N$ values indicate that the nitrate is of organic origin, the spring ratio (+7.3 per mil) is heavier than the ratio in the fall (0.3 per mil), possibly indicating that microbial activity has fractionated the nitrate by denitrification. Dissolved oxygen during the spring was 0.9 mg/L (close to anaerobic conditions),

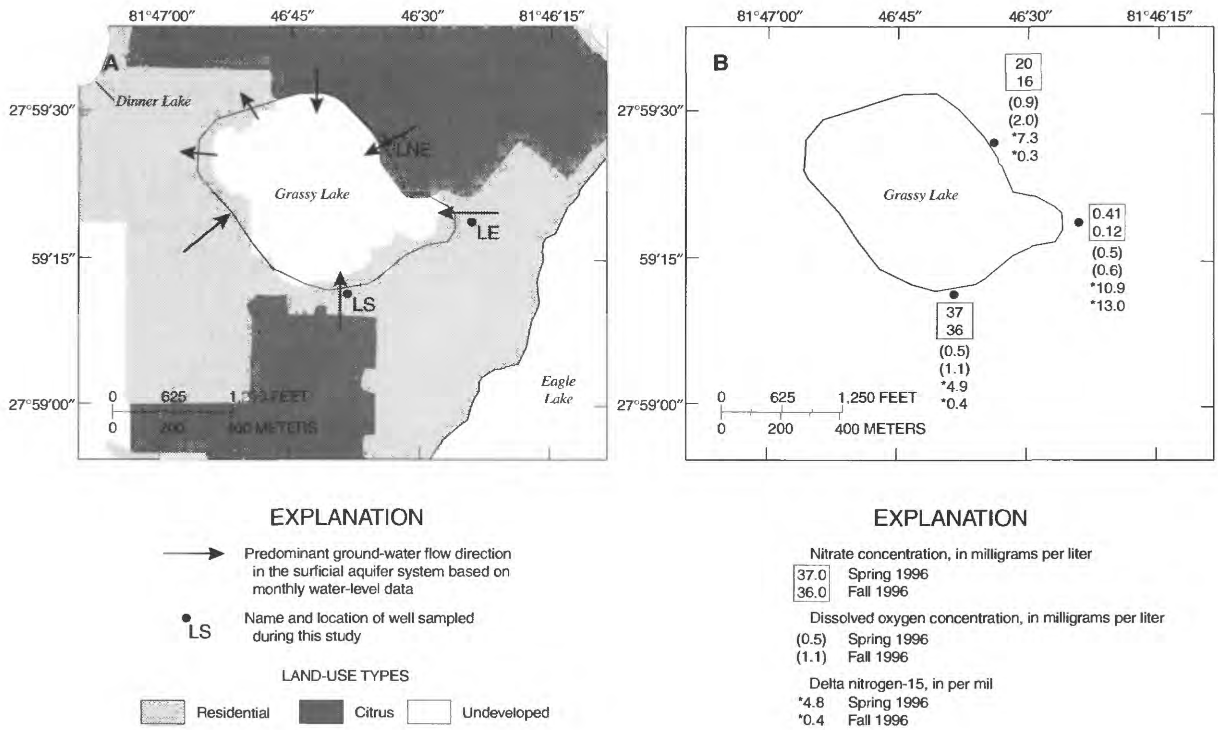


Figure 10. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for Lake Isis and for water from surficial aquifer system wells, Grassy Lake basin, Polk County, Florida.

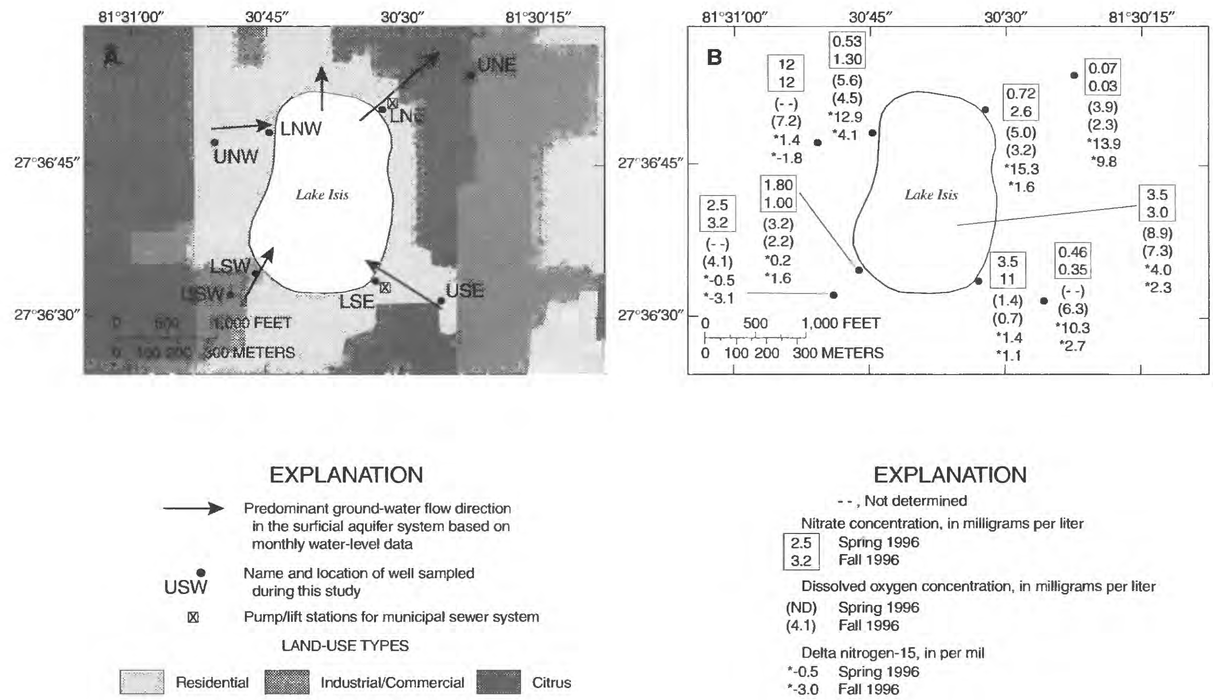


Figure 11. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Lake Isis basin, Highlands County, Florida.

whereas in the fall it was 2.0 mg/L (aerobic conditions). The influence of the fluctuating aerobic/anaerobic conditions in the ground water might have affected the $\delta^{15}N$ values.

At the LS well, the affect of varying redox conditions also was observed. The dissolved oxygen concentration during the spring sampling was 0.5 mg/L (virtually anaerobic) and the nitrogen isotope signature was +4.9 per mil. During the fall, dissolved oxygen was 1.1 mg/L, indicating that probably little anaerobic microbial activity occurs to alter the isotopic signature; the $\delta^{15}N$ is lighter at +0.4 per mil (closer to an original signature of fertilizer). Although the $\delta^{15}N$ values within this lake basin appear to be affected by microbial fractionation, the difference between inorganic and organic sources remains distinguishable using $\delta^{15}N$ signatures.

Residential land use is present near the shoreline of Lake Isis (fig. 11), but citrus agriculture and industrial land-use areas surround the lake in the upper parts of the lake basin. Residential properties are connected to municipal sewer lines and associated sewer pump/lift stations are located along the edge of the lake (fig 11a). Leaking pipes associated with these lift stations might be a source of nitrate in ground water. Citrus agriculture is located further from the shore at Lake Isis, compared to closer to the lake at Grassy Lake and Lake Starr. However, Lake Isis is deeper (maximum depth more than 60 ft) than Grassy Lake and Lake Starr (maximum depths about 20 and 30 ft, respectively), and the surficial aquifer system intersects Lake Isis at a greater depth.

Ground-water inflow to Lake Isis occurs along flow paths near wells USE, USW, LSW, UNW, and LNW. Lake leakage into the surficial aquifer system likely occurs at the UNE and LNE wells. Nitrate concentrations in water from these wells ranged from 0.03 to 2.6 mg/L. Nitrate concentrations in the lake water were 3.5 mg/L in the spring and 3.0 mg/L in the fall. Nearly all the ground water had measurable dissolved oxygen concentrations, indicating little chance for nitrate removal by anaerobic microbial processes throughout the basin. The $\delta^{15}N$ signatures of the ground-water samples ranged from -3.0 to +15.3 per mil, and the lake $\delta^{15}N$ values were +4.0 to +2.3 per mil in the spring and fall, respectively. Citrus agricultural activity is east, west and southwest of Lake Isis, at the outer edges of the lake's topographic drainage basin. The $\delta^{15}N$ values in water from wells USW, LSW, and UNW suggest that inorganic (fertilizer) nitrate is a probable source. Generally, nitrate levels are higher in these ground waters than in the rest of the basin (fig. 11b). The lower southeast (LSE) well, downgradient from an area of citrus agriculture, is an exception to this general trend. This well is near a pump/lift station for the municipal sewer system. The $\delta^{15}N$ values (+1.6 to 15.3 per mil) in water from the LNW, LNE, UNE and USE wells indicate the influence of an organic source of nitrate. During the spring, these signatures are heavier (+4.1 to +13.9 per mil) and are likely due to an organic source, although the nitrate concentrations are not above 3.0 mg/L. The UNE and LNE wells are downgradient from the lake and might reflect an influence of lake water and ground-water movement through anaerobic lake-bottom sediments where nitrate can be removed by biological processes.

The shoreline of Lake Starr (fig. 12a) is surrounded by residential land use (with septic development along the lake shore), but the upper parts of the basin are dominated by citrus agricultural activity. Some commercial/industrial land use is present west of the lake, but is a very small percentage of the overall land use within the basin. Seepage of lake water into the surficial aquifer system occurs along the south and southwestern shore of the lake, probably controlled by localized subsidence features in this area. Within the Lake Starr basin, the land use is highly compartmentalized because many residential homeowners have their own citrus groves located on adjacent properties (fig. 12a).

Ground-water inflow to Lake Starr occurs along flow paths near wells LW, LNW, UN, LN, UE, and LE. Ground-water outflow occurs along the southern shore of Lake Starr, where LSE and USE wells are located. Nitrate concentrations in water from the eight wells near Lake Starr ranged from less than 0.02 to 16 mg/L. The $\delta^{15}N$ values ranged from -7.0 to + 12.6 per mil (fig. 12b).

Generally, water from wells in the Lake Starr basin had light $\delta^{15}N$ signatures, indicating an inorganic source of nitrate. Dissolved oxygen

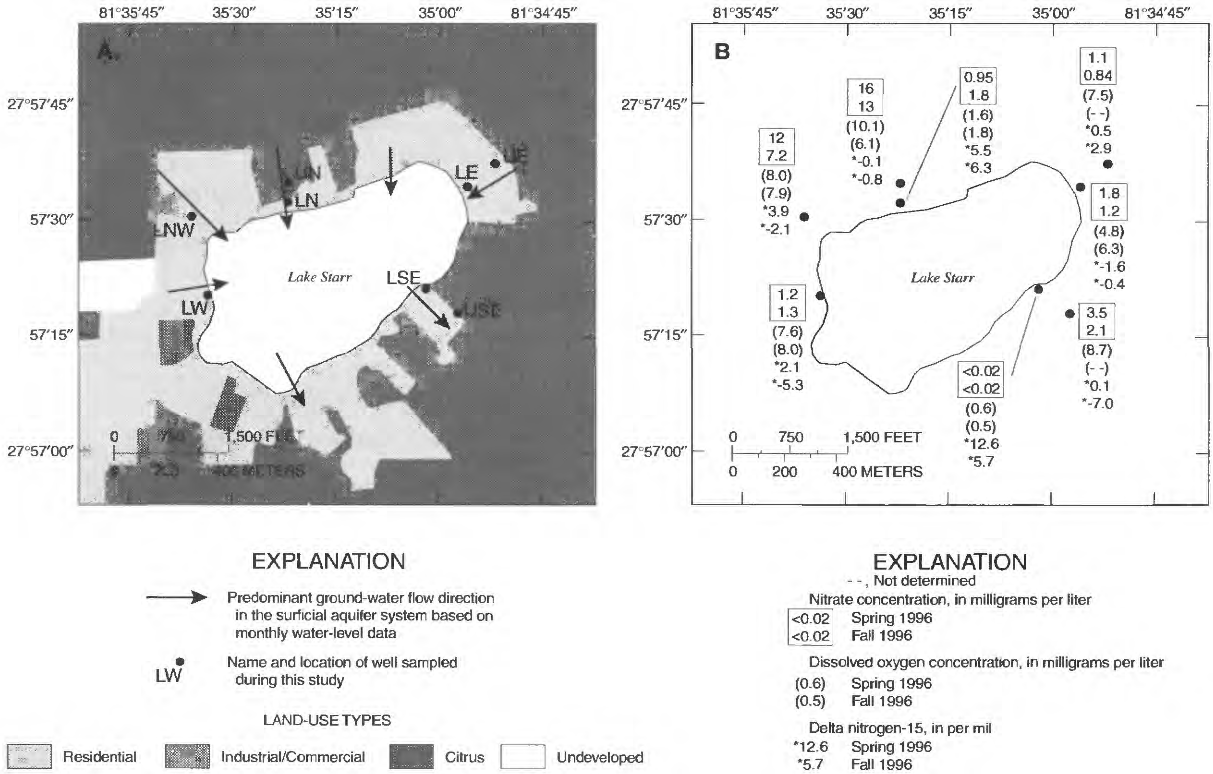


Figure 12. (A) Land use and predominant ground-water flow patterns within the surficial aquifer system, and (B) nitrate, dissolved oxygen, and nitrogen-15 data for water from surficial aquifer system wells, Lake Starr basin, Polk County, Florida.

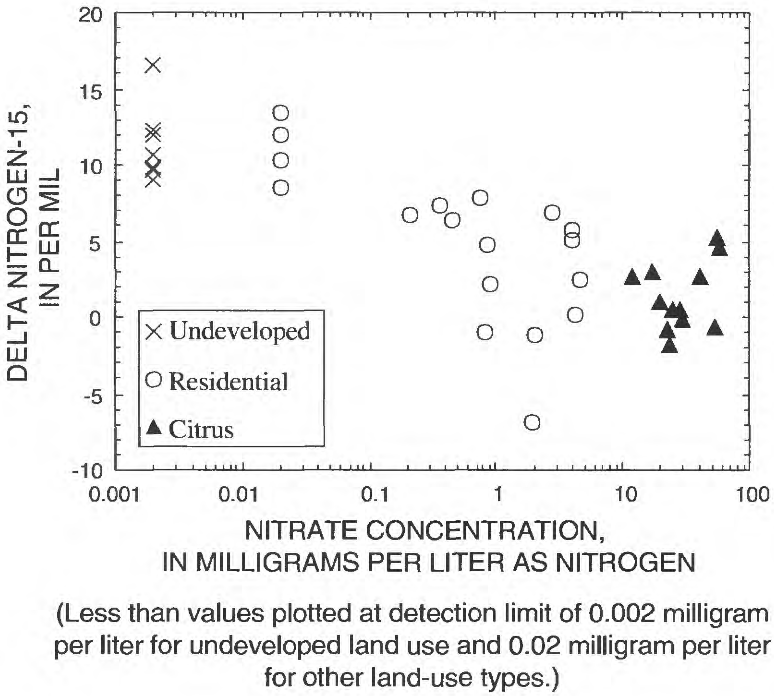


Figure 13. Relation between delta nitrogen-15 ($\delta^{15}N$) and nitrate concentrations in ground-water samples collected from wells located in undeveloped, citrus, and residential land-use areas, Central Lakes District, Polk and Highlands Counties, Florida.

concentrations in these waters were also high. Where dissolved oxygen concentrations were low (less than 2 mg/L), $\delta^{15}N$ values were heavier (wells LN and LSE), suggesting both microbial fractionation and the contribution of an organic source of nitrate (probably residential, septic-tank leachate).

At the LN well, the $\delta^{15}N$ values ranged from +5.5 to +6.3 per mil. Although this range is not indicative solely of an organic source, it is heavier than the light values observed in the upgradient UN well (-0.1 and -0.8 per mil). The UN well is within a citrus grove; the LN well is within a residential property near the lakeshore. Mixing of various nitrate sources probably occurs between these wells. The increasingly heavier $\delta^{15}N$ values between the UN and LN wells is evidence that there is an influence of an organic source of nitrate. The presence of dissolved oxygen in water from both wells indicates that little denitrification occurs along this flow path.

Lake leakage occurs along the flow path through the LSE well. Water from this well probably reflects lake-water isotopic signatures. Water from this well is characterized by very low nitrate concentrations (less than 0.02 mg/L), low dissolved oxygen concentrations (less than 1 mg/L), and heavier isotopic signatures (greater than +5 per mil). This indicates that anaerobic microbial activity might have contributed to the fractionation of a nitrate source. Although the lake water probably is affected by both inorganic and organic sources of nitrogen, when anaerobic conditions persist, nitrate concentrations are reduced.

Relation Between Nitrogen-Isotope Signatures, Nitrate, and Land Use

Generally, the sources of nitrate within the surficial aquifer system at the nine selected lake basins can be distinguished from one another by using nitrogen isotope ratios. In lake basins that are predominantly of either undeveloped or citrus land-use type, the relation between $\delta^{15}N$ signatures and nitrate concentrations corresponds to land-use type (fig. 13, above). Ground water from lake basins with citrus land use has the highest concentrations of nitrate and its nitrogen isotopic signature is generally less than 5 per mil. Although citrus land use corresponds to the highest nitrate concentrations of inorganic origin, some areas of residential land use also seem to be influenced strongly by inorganic fertilizer signatures, but ground water from these areas has lower nitrate concentrations. Undeveloped lake basins have heavier isotopic signatures, in the range of organic sources, but nitrate concentrations are low, indicating that natural nitrate present has been reduced.

In basins with mixed land use, the $\delta^{15}N$ signatures also can help to delineate nitrate sources. Sampling sites for lake basins with a mixture of land use types were assigned a subtype land-use category based on the land use observed within the contributing recharge area for each sampling site. The relation between $\delta^{15}N$ and nitrate concentrations in ground water was plotted for these subtypes (fig. 14). Although there is some overlap of $\delta^{15}N$ signatures for ground water from the three different land-use types, ground water from citrus land-use areas typically has lighter $\delta^{15}N$ values (usually less than +1 per mil) and higher nitrate concentrations (generally greater than 10 mg/L). Ground water from residential land-use types has both high and low $\delta^{15}N$ values, probably reflecting two different sources for nitrate; the higher nitrate concentrations correspond to fertilizer (lighter) sources, whereas ground water from some residential sites with nitrate concentrations below 1 mg/L can indicate a heavier organic source of nitrate. Sources of nitrate can be distinguished within mixed land-use basins if adjacent land use and predominant ground-water flow directions are known.

The redox state of the ground water exerts a strong influence on the concentration of nitrate in ground water regardless of the initial source. The highest ground-water nitrate concentrations were found where dissolved oxygen levels are highest. Lower nitrate concentrations were measured where dissolved oxygen levels in ground water are lower. In the latter case, where microbial reduction of nitrate might occur, nitrate concentrations are low and the nitrogen isotope signatures typically range from 0 to +10 per mil, even though there can be an original inorganic source of lighter nitrogen. However, these signatures do not seem to be fractionated above +10 per mil such that they could be interpreted as having an organic source. This apparent relation between the aerobic state of the ground water and the corresponding nitrate concentrations is shown in figure 15. Citrus land use is associated with the highest nitrate concentrations, but this is partly because citrus cultivation is located in well-drained upland areas. Ground water

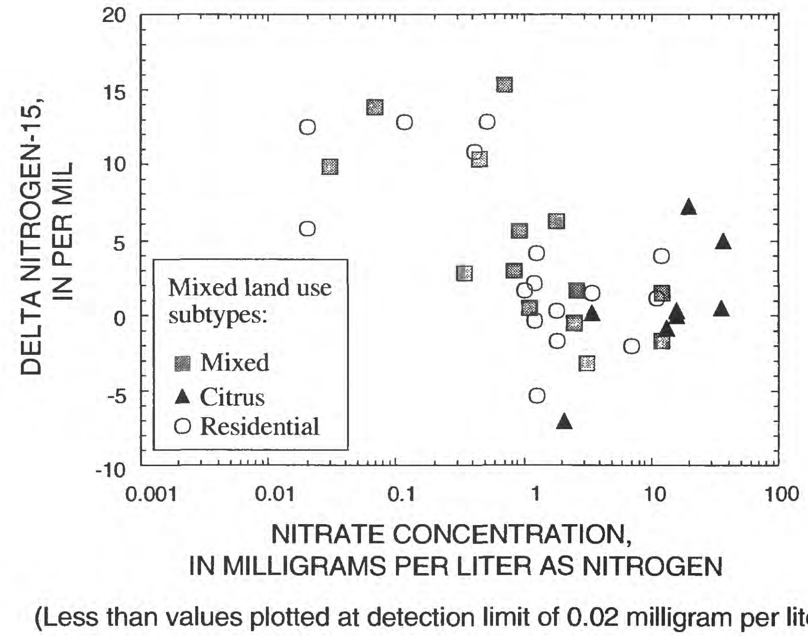
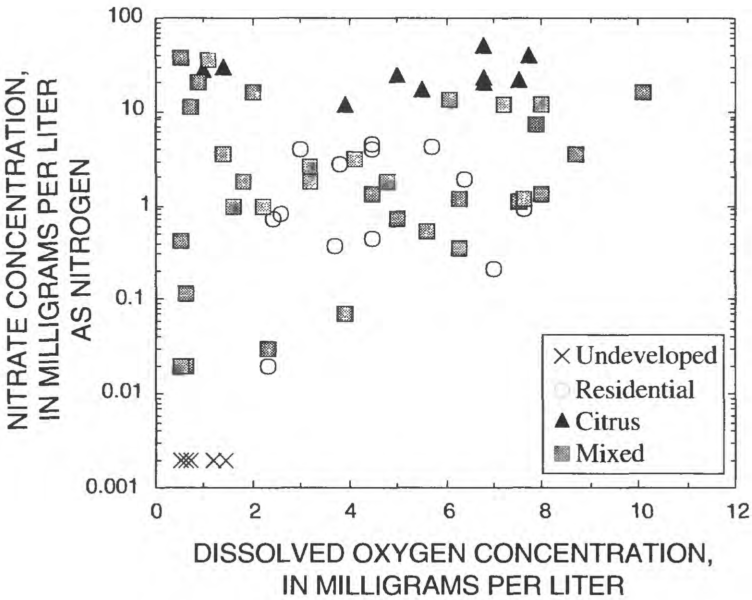


Figure 14. Relation between delta nitrogen-15 ($\delta^{15}N$) and nitrate concentrations in ground-water samples collected from wells located in lake basins having mixed land-use types, Central Lakes District, Polk and Highlands Counties, Florida.



(Less than values for nitrate plotted at detection limit of 0.002 milligram per liter for undeveloped land use and 0.02 milligram per liter for other land-use types.)

Figure 15. Relation between nitrate and dissolved oxygen concentrations in all ground-water samples collected from wells in lake basins located in undeveloped, citrus, residential, and mixed land-use areas, Central Lakes District, Polk and Highlands Counties, Florida.

beneath these areas typically is aerobic and, therefore, conducive to nitrate accumulation. Several ground-water samples had elevated nitrate concentrations despite having dissolved oxygen concentrations of less than 2.0 mg/L (fig. 14). These samples correspond to citrus and mixed land-use areas, where a significant fertilizer source (citrus or residential) is near the lake shoreline. The $\delta^{15}N$ signatures of these samples suggest that some fractionation of the nitrate is occurring, but nitrate concentrations have not been lowered significantly by microbial reduction, possibly because fertilizer applications contribute nitrate at rates exceeding rates of nitrate reduction caused by denitrification reactions.

SUMMARY AND CONCLUSIONS

The nitrogen-isotope technique is a useful way to distinguish between organic and inorganic sources of nitrate and denitrification processes in ground water within lake basins in the Central Lakes District of Polk and Highlands Counties, Florida. Possible fractionation processes that alter the original signature of the nitrogen source do not seem to compromise the interpretation of the $\delta^{15}N$ data. The $\delta^{15}N$ data, especially if collected in conjunction with other hydrologic and chemical data, can provide insight to the processes that occur within the surficial aquifer system of a lake basin. In the nine lake basins of this study where ground-water nitrate concentrations are elevated, the most significant source of nitrate, as determined from $\delta^{15}N$ signatures, is inorganic nitrogen (fertilizers). The aerobic state of the ground water plays a major role in providing conditions that either favor the persistence of nitrate or facilitate natural remediation of ground-water nitrate by denitrification. In ground water from nine lake basins, areas with low dissolved oxygen concentrations corresponded to areas where lower nitrate concentrations existed. Citrus agricultural land use, traditionally located in well-drained areas where the ground water is oxygen-rich, had the highest concentrations of nitrate and the lightest $\delta^{15}N$ values, indicating that little to no microbial fractionation of nitrogen species had occurred. In contrast, areas where organic sources of nitrate were likely to exist, as indicated by nitrogen-isotope signatures, nitrate concentrations were lower. Generally, as ground water moves downgradient (along a flow path), $\delta^{15}N$ signatures become heavier, corresponding to a decrease in dissolved oxygen concentrations. These heavier $\delta^{15}N$ signatures indicate that soils or sediments adjacent to lake shorelines may contain more organic soil nitrate and that microbial fractionation likely occurs.

Nitrogen-isotope data indicate that nitrate from septic-tank systems can be converted to other nitrogen species by microbial populations and, therefore, does not reach higher nitrate concentrations found in ground water beneath areas of citrus agricultural land use. The lower nitrate concentrations may be due to several factors, including the anaerobic state of the water, the presence of an appropriate microbial population, and low nitrate loading rates. Septic-tank system nutrient loads can be lower than fertilizer application rates, especially with respect to the areal distribution of the nitrate source. A lack of elevated nitrate concentrations in ground water beneath residential areas that use septic tanks indicates that the septic tank and drain field probably are effective in reducing nitrate concentrations before leachate reaches the surficial aquifer system.

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Appendix

Appendix. Chemical and isotopic data from water samples collected at nine selected lake basins, Central Lakes District, Polk and Highlands Counties, Florida, 1996

[mg/L, milligrams per liter; N, nitrogen; µS/cm, microsiemens per centimeter; <, less than; --, not available]

Lake basin	Well name	Sampling date (Year/Mo/Day)	Lake basin land-use type	Delta nitrogen-15 ($\delta^{15}N$) (per mil)	Nitrogen, nitrate (NO_3), dissolved (mg/L as N)	Nitrogen, nitrite (NO_2), dissolved (mg/L as N)	Nitrogen, ammonia (NH_4), dissolved (mg/L as N)
Annie	LS	1996/04/09	undeveloped	12.3	< 0.002	0.007	0.03
Annie	LS	1996/10/15	undeveloped	9.7	< 0.002	0.004	0.03
Annie	LW	1996/04/08	undeveloped	16.6	< 0.002	0.003	0.03
Annie	LW	1996/10/15	undeveloped	9.8	< 0.002	0.003	0.04
Grassy	LE	1996/04/29	mixed	10.9	0.41	0.010	0.02
Grassy	LE	1996/10/31	mixed	13.0	0.12	0.012	0.03
Grassy	LNE	1996/04/25	mixed	7.3	20	< 0.01	0.02
Grassy	LNE	1996/10/31	mixed	0.3	16	< 0.01	< 0.01
Grassy	LS	1996/04/25	mixed	4.9	37	< 0.01	0.02
Grassy	LS	1996/10/30	mixed	0.4	36	0.018	< 0.01
Hollingsworth	LNW	1996/05/02	residential	6.4	0.45	< 0.01	0.04
Hollingsworth	LNW	1996/11/05	residential	7.4	0.37	< 0.01	0.02
Hollingsworth	LS	1996/05/06	residential	2.4	4.6	< 0.01	0.04
Hollingsworth	LS	1996/11/05	residential	0.1	4.2	< 0.01	< 0.01
Hollingsworth	LW	1996/05/02	residential	6.8	2.8	0.050	< 0.01
Hollingsworth	LW	1996/11/06	residential	5.7	4.0	0.070	< 0.01
Hollingsworth	UNW	1996/05/07	residential	4.8	0.84	--	0.05
Hollingsworth	UNW	1996/11/05	residential	7.9	0.74	< 0.01	0.05
Hollingsworth	UW	1996/05/06	residential	-1.2	2.0	--	0.05
Hollingsworth	UW	1996/11/06	residential	-6.8	1.9	< 0.01	0.03
Isis	LNE	1996/04/10	mixed	15.3	0.72	< 0.01	0.01
Isis	LNE	1996/10/16	mixed	1.6	2.6	< 0.01	< 0.01
Isis	LNW	1996/04/10	mixed	12.9	0.53	< 0.01	< 0.01
Isis	LNW	1996/10/17	mixed	4.1	1.3	< 0.01	< 0.01
Isis	LSE	1996/04/09	mixed	1.4	3.5	< 0.01	0.01
Isis	LSE	1996/10/16	mixed	1.1	11	< 0.01	< 0.01
Isis	LSW	1996/04/10	mixed	0.2	1.8	< 0.01	< 0.01
Isis	LSW	1996/10/16	mixed	1.6	1.0	< 0.01	< 0.01
Isis	UNE	1996/04/10	mixed	13.9	0.07	--	0.02
Isis	UNE	1996/10/16	mixed	9.8	0.03	< 0.01	< 0.01
Isis	UNW	1996/04/10	mixed	1.4	12	--	0.01
Isis	UNW	1996/10/17	mixed	-1.8	12	< 0.01	0.01
Isis	USE	1996/04/09	mixed	10.3	0.46	--	0.03
Isis	USE	1996/10/16	mixed	2.7	0.35	< 0.01	0.02
Isis	USW	1996/04/10	mixed	-0.5	2.5	--	0.02
Isis	USW	1996/10/16	mixed	-3.1	3.2	< 0.01	0.01
Lake Isis	--	1996/04/03	lake	4.0	3.5	0.020	0.02
Lake Isis	--	1996/10/01	lake	2.3	3.0	0.021	< 0.01

Appendix. Chemical and isotopic data from water samples collected at nine selected lake basins, Central Lakes District, Polk and Highlands Counties, Florida, 1996--Continued

[mg/L, milligrams per liter; N, nitrogen; µS/cm, microsiemens per centimeter; <, less than; --, not available]

Lake basin	Well name	Nitrogen, ammonia (NH_4) + organic N, dissolved (mg/L as N)	Oxygen, dissolved (mg/L)	Field pH (standard units)	Specific conductance, field (µS/cm)	U.S. Geological Survey identification number
Annie	LS	0.55	1.2	4.15	65	271214081210501
Annie	LS	0.36	0.6	4.24	58	271214081210501
Annie	LW	0.35	1.4	3.93	72	271218081211601
Annie	LW	0.27	< 0.5	4.03	66	271218081211601
Grassy	LE	0.79	< 0.5	6.34	148	275919081462501
Grassy	LE	0.60	0.6	6.43	115	275919081462501
Grassy	LNE	0.41	0.9	4.46	321	275926081463501
Grassy	LNE	0.37	2.0	4.42	266	275926081463501
Grassy	LS	0.57	< 0.5	5.49	551	275913081463901
Grassy	LS	< 0.20	1.1	5.51	517	275913081463901
Hollingsworth	LNW	< 0.20	4.5	4.40	244	280141081570001
Hollingsworth	LNW	< 0.20	3.7	4.49	230	280141081570001
Hollingsworth	LS	< 0.20	4.5	4.64	120	280107081565901
Hollingsworth	LS	< 0.20	5.7	4.47	118	280107081565901
Hollingsworth	LW	0.24	3.8	6.52	312	280136081570901
Hollingsworth	LW	0.44	4.5	6.45	311	280136081570901
Hollingsworth	UNW	< 0.20	--	4.87	81	280157081565901
Hollingsworth	UNW	0.43	2.4	4.91	88	280157081565901
Hollingsworth	UW	0.22	--	5.40	74	280134081572201
Hollingsworth	UW	0.37	6.4	4.92	69	280134081572201
Isis	LNE	< 0.20	5.0	6.32	204	273652081303001
Isis	LNE	< 0.20	3.2	6.54	223	273652081303001
Isis	LNW	< 0.20	5.6	5.47	81	273649081304501
Isis	LNW	< 0.20	4.5	5.24	84	273649081304501
Isis	LSE	< 0.20	1.4	4.60	159	273636081303101
Isis	LSE	< 0.20	0.7	4.39	282	273636081303101
Isis	LSW	< 0.20	3.2	4.87	75	273636081304501
Isis	LSW	< 0.20	2.2	5.20	87	273636081304501
Isis	UNE	< 0.20	3.9	4.80	61	273653081302201
Isis	UNE	< 0.20	2.3	4.76	67	273653081302201
Isis	UNW	< 0.20	--	5.88	327	273648081305101
Isis	UNW	< 0.20	7.2	5.87	318	273648081305101
Isis	USE	< 0.20	--	5.01	37	273635081302601
Isis	USE	< 0.20	6.3	4.87	46	273635081302601
Isis	USW	< 0.20	--	4.66	79	273633081304801
Isis	USW	< 0.20	4.1	4.58	104	273633081304801
Lake Isis	--	0.20	8.9	6.74	207	273635081303400
Lake Isis	--	< 0.20	7.3	7.65	216	273635081303400

Appendix. Chemical and isotopic data from water samples collected at nine selected lake basins, Central Lakes District, Polk and Highlands Counties, Florida, 1996--Continued

[mg/L, milligrams per liter; N, nitrogen; µS/cm, microsiemens per centimeter; <, less than; --, not available].

Lake basin	Well name	Sampling date (Year/Mo/Day)	Lake basin land-use type	Delta nitrogen-15 ($\delta^{15}N$) (per mil)	Nitrogen, nitrate (NO_3), dissolved (mg/L as N)	Nitrogen, nitrite (NO_2), dissolved (mg/L as N)	Nitrogen, ammonia (NH_4), dissolved (mg/L as N)
Olivia	LS	1996/04/11	residential	13.4	< 0.02	< 0.01	0.09
Olivia	LS	1996/10/21	residential	8.5	< 0.02	< 0.01	0.12
Olivia	UNW	1996/04/11	residential	2.1	0.91	--	0.01
Olivia	UNW	1996/10/22	residential	6.7	0.21	< 0.01	< 0.01
Olivia	US	1996/04/11	residential	12.0	< 0.02	--	0.08
Olivia	US	1996/10/21	residential	10.4	< 0.02	< 0.01	0.10
Olivia	USW	1996/04/11	residential	5.1	4.0	--	0.01
Olivia	USW	1996/10/22	residential	-1.0	0.82	< 0.01	< 0.01
Round	LN	1996/04/23	citrus	2.6	12	< 0.01	0.07
Round	LN	1996/10/29	citrus	0.5	24	< 0.01	0.02
Round	LSE	1996/04/24	citrus	0.5	28	< 0.01	0.01
Round	LSE	1996/10/30	citrus	-0.1	30	< 0.01	< 0.01
Round	UN	1996/04/23	citrus	5.3	55	--	0.03
Round	UN	1996/10/29	citrus	2.6	40	< 0.01	0.03
Round	USE	1996/04/24	citrus	4.7	57	--	0.02
Round	USE	1996/10/29	citrus	-0.7	52	< 0.01	0.05
Saddle Blanket	LSE	1996/04/16	undeveloped	12.0	< 0.002	< 0.001	0.09
Saddle Blanket	LSE	1996/10/23	undeveloped	12.0	< 0.002	0.012	0.06
Saddle Blanket	LSW	1996/04/16	undeveloped	10.6	< 0.002	< 0.001	0.22
Saddle Blanket	LSW	1996/10/23	undeveloped	9.0	< 0.002	0.004	0.17
Starr	LE	1996/04/22	mixed	-1.6	1.8	< 0.01	0.01
Starr	LE	1996/10/28	mixed	-0.4	1.2	< 0.01	< 0.01
Starr	LN	1996/04/22	mixed	5.5	0.95	< 0.01	0.01
Starr	LN	1996/10/28	mixed	6.3	1.8	< 0.01	0.01
Starr	LNW	1996/04/18	mixed	3.9	12	< 0.01	0.01
Starr	LNW	1996/10/28	mixed	-2.1	7.2	< 0.01	< 0.01
Starr	LSE	1996/04/18	mixed	12.6	< 0.02	< 0.01	0.06
Starr	LSE	1996/10/28	mixed	5.7	< 0.02	< 0.01	0.63
Starr	LW	1996/04/17	mixed	2.1	1.2	< 0.01	0.01
Starr	LW	1996/10/24	mixed	-5.3	1.3	< 0.01	0.01
Starr	UE	1996/04/22	mixed	0.5	1.1	--	0.02
Starr	UE	1996/10/28	mixed	2.9	0.84	< 0.01	0.02
Starr	UN	1996/04/22	mixed	-0.1	16	--	0.01
Starr	UN	1996/10/28	mixed	-0.8	13	< 0.01	0.03
Starr	USE	1996/04/22	mixed	0.1	3.5	--	0.01
Starr	USE	1996/10/28	mixed	-7.0	2.1	< 0.01	0.02
Swim	LNE	1996/04/17	citrus	0.9	20	< 0.01	0.01
Swim	LNE	1996/10/10	citrus	3.0	17	< 0.01	< 0.01
Swim	LSE	1996/04/17	citrus	-0.9	22	< 0.01	0.06
Swim	LSE	1996/10/10	citrus	-1.8	23	< 0.01	< 0.01
Swim Lake	--	1996/04/03	lake	10.9	10	0.050	0.02
Swim Lake	--	1996/10/02	lake	6.4	4.9	0.032	0.03

Appendix. Chemical and isotopic data from water samples collected at nine selected lake basins, Central Lakes District, Polk and Highlands Counties, Florida, 1996--Continued

[mg/L, milligrams per liter; N, nitrogen; µS/cm, microsiemens per centimeter; <, less than; --, not available]

Lake basin	Well name	Nitrogen, ammonia (NH_4) + organic N, dissolved (mg/L as N)	Oxygen, dissolved (mg/L)	Field pH (standard units)	Specific conductance, field (µS/cm)	U.S. Geological Survey identification number
Olivia	LS	0.67	< 0.5	5.85	65	273746081324701
Olivia	LS	0.65	< 0.5	5.75	81	273746081324701
Olivia	UNW	< 0.20	7.6	5.39	48	273808081325901
Olivia	UNW	0.25	7.0	4.96	28	273808081325901
Olivia	US	0.21	--	5.16	54	273730081324701
Olivia	US	0.38	2.3	5.10	37	273730081324701
Olivia	USW	< 0.20	3.0	4.78	100	273746081330801
Olivia	USW	0.23	2.6	4.94	51	273746081330801
Round	LN	0.35	3.9	4.53	275	275753081402501
Round	LN	0.27	5.0	4.55	375	275753081402501
Round	LSE	< 0.20	1.0	4.26	365	275742081402201
Round	LSE	< 0.20	1.4	4.12	381	275742081402201
Round	UN	0.53	--	4.34	611	275755081402501
Round	UN	0.27	7.7	4.33	516	275755081402501
Round	USE	0.38	--	4.31	840	275738081402001
Round	USE	0.51	6.8	4.17	745	275738081402001
Saddle Blanket	LSE	0.91	0.7	3.82	91	274005081342401
Saddle Blanket	LSE	0.80	0.5	3.95	59	274005081342401
Saddle Blanket	LSW	0.36	0.6	4.43	94	274005081343101
Saddle Blanket	LSW	0.40	0.6	4.47	92	274005081343101
Starr	LE	< 0.20	4.8	4.91	46	275734081345501
Starr	LE	0.26	6.3	4.86	37	275734081345501
Starr	LN	< 0.20	1.6	5.12	213	275734081352301
Starr	LN	< 0.20	1.8	5.03	195	275734081352301
Starr	LNW	< 0.20	8.0	4.23	218	275729081353701
Starr	LNW	< 0.20	7.9	4.22	167	275729081353701
Starr	LSE	0.46	0.6	5.80	105	275721081350301
Starr	LSE	0.93	< 0.5	5.68	106	275721081350301
Starr	LW	< 0.20	7.6	6.65	153	275719081353401
Starr	LW	0.26	8.0	6.87	101	275719081353401
Starr	UE	0.40	7.5	4.74	61	275737081345101
Starr	UE	< 0.20	--	4.65	64	275737081345101
Starr	UN	0.24	10.1	4.46	313	275736081352301
Starr	UN	0.25	6.1	4.52	332	275736081352301
Starr	USE	0.20	8.7	4.82	158	275717081345801
Starr	USE	0.25	--	4.76	150	275717081345801
Swim	LNE	< 0.20	6.8	4.75	280	275403081285101
Swim	LNE	< 0.20	5.5	4.61	261	275403081285101
Swim	LSE	0.34	7.5	4.23	366	275359081284901
Swim	LSE	< 0.20	6.8	4.25	349	275359081284901
Swim Lake	--	0.39	8.9	8.65	325	275403081285400
Swim Lake	--	0.36	6.4	7.71	304	275403081285400