JOURNAL OF THE AMERICAN WATER RESOURCES ASSOCIATION

Vol. 45, No. 3 AMERICAN WATER RESOURCES ASSOCIATION June 2009

ESTIMATING NITROGEN LOADING TO GROUND WATER AND ASSESSING VULNERABILITY TO NITRATE CONTAMINATION IN A LARGE KARSTIC SPRINGS BASIN, FLORIDA[1]

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ABSTRACT: A nitrogen (N) mass-balance budget was developed to assess the sources of N affecting increasing ground-water nitrate concentrations in the 960-km^2 karstic Ichetucknee Springs basin. This budget included direct measurements of N species in rainfall, ground water, and spring waters, along with estimates of N loading from fertilizers, septic tanks, animal wastes, and the land application of treated municipal wastewater and residual solids. Based on a range of N leaching estimates, N loads to ground water ranged from 262,000 to 1.3 million kg/year; and were similar to N export from the basin in spring waters (266,000 kg/year) when 80-90% N losses were assumed. Fertilizers applied to cropland, lawns, and pine stands contributed about 51% of the estimated total annual N load to ground water in the basin. Other sources contributed the following percentages of total N load to ground water: animal wastes, 27%; septic tanks, 12%; atmospheric deposition, 8%; and the land application of treated wastewater and biosolids, 2%. Due to below normal rainfall (97.3 cm) during the 12-month rainfall collection period, N inputs from rainfall likely were about 30% lower than estimates for normal annual rainfall (136 cm). Low N-isotope values for six spring waters ($\delta^{15}N\text{-}NO_3$ = 3.3 to 6.3‰) and elevated potassium concentrations in ground water and spring waters were consistent with the large N contribution from fertilizers. Given ground-water residence times on the order of decades for spring waters, possible sinks for excess N inputs to the basin include N storage in the unsaturated zone and parts of the aquifer with relatively sluggish ground-water movement and denitrification. A geographical-based model of spatial loading from fertilizers indicated that areas most vulnerable to nitrate contamination were located in closed depressions containing sinkholes and other dissolution features in the southern half of the basin.

(KEY TERMS: nitrogen; nonpoint source pollution; isotopes; geospatial analysis; ground-water management; Florida; Ichetucknee.)

Katz, Brian G., A. Alejandro Sepulveda, and Richard J. Verdi, 2009. Estimating Nitrogen Loading to Ground Water and Assessing Vulnerability to Nitrate Contamination in a Large Karstic Springs Basin, Florida. *Journal of the American Water Resources Association* (JAWRA) 45(3):607-627. DOI: 10.1111/j.1752-1688.2009.00309.x

INTRODUCTION

Ground water in karstic spring basins worldwide is particularly vulnerable to nitate contamination from anthropogenic activities at the land surface (Drew and Hotzl, 1999). Numerous sinkholes, disappearing streams, and conduit systems associated with large springs allow for relatively rapid movement of contaminants from the land surface to the ground-water

[1]Paper No. JAWRA-08-0130-P of the *Journal of the American Water Resources Association* (JAWRA). Received July 7, 2008; accepted October 1, 2008. **Discussions are open until six months from print publication.**

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system with little attenuation or degradation. Elevated nitrate concentrations in ground water have raised both human and ecological health concerns. Human health issues associated with nitrate in drinking water include methemoglobinemia (Johnson *et al.*, 1987), and several types of cancer (Ward *et al.*, 1996, 2005; Weyer *et al.*, 2001; DeRoos *et al.*, 2003). Recent studies indicate that nitrate may affect various metabolic processes in fishes and reptiles through disruption of hormone synthesis (Edwards, 2005; Guillette and Edwards, 2005). Enriched nitrate concentrations also may be affecting the global decline in amphibian populations (Rouse *et al.*, 1999). Even when nitrate-N concentrations in ground water are below the maximum contaminant level of 10 mg/l for drinking water (USEPA, 1988), low nitrate-N concentrations (0.6-1.5 mg/l) in spring waters can stimulate the growth of cyanobacterial biomass (Cowell and Dawes, 2004). Muir *et al.* (1991) showed that *Penaeus monodon* protozoea exhibited "significant mortality" at nitrate-N concentrations as low as 0.23 mg/l. Springs discharge large loads of N to surface waters (Pittman *et al.*, 1997), and nuisance levels of algae and macrophytes occur in many spring-fed rivers in Florida (Jones *et al.*, 1996; Hornsby and Mattson, 1998; Florida Springs Task Force, 2000). Although many springs in Florida and elsewhere have nitrate-N concentrations exceeding 0.1 mg/l (background N concentration) (Katz, 1992; Maddox *et al.*, 1992), there are no guidelines for nitrate-N concentrations in spring-fed streams to limit the growth of nuisance aquatic vegetation.

Potential contributors of nitrate to ground water in spring basins include fertilizers, atmospheric deposition, livestock, septic systems, and land application of municipal wastewater and biosolids. Determining the dominant sources of nitrate inputs to highly vulnerable karstic spring basins provides information for making more effective management decisions about alleviating nitrate contamination of ground water. Relative contributions from various N sources can differ considerably depending on dominant land-use activities. Fertilizers contributed about 70% of the total mass of N in two agriculturally-dominated spring basins in a sinkhole plain in southwestern Illinois; although Panno and Kelly (2004) estimated that slightly more than half of the nitrate discharged from springs was from background sources and the remainder from fertilizers. Chelette *et al.* (2002) estimated that the land application of municipal wastewater and solids, and on-site waste disposal systems contributed the dominant nitrate-N load (61% of total N) in the 388-km^2 basin for Wakulla Springs, a large karstic spring in northern Florida. In the 1,680-km^2 Wekiva Springs basin in central Florida, where land use is forested (52%), residential (21%), and agricultural (18%), fertilizers contributed about 54% of the N load, whereas septic-tank and municipal wastewater sources contributed about 32% (MACTEC, 2007).

Nitrate-N concentrations have steadily increased during the past 40 years in many spring waters within the Suwannee River basin in Florida (Upchurch *et al.*, 2007). Fertilizer inputs to the land surface were found to be a dominant source of N in the lower basin during the period, 1940-1998 (Katz *et al.*, 1999). Trends in spring water nitrate-N concentrations were consistent with a peak in county-wide fertilizer usage in the 1970s; however, spring water responses to these inputs have been subdued and delayed because average ground-water residence times are on the order of decades (Katz *et al.*, 2001).

This paper presents a comprehensive N mass-balance budget for the Ichetucknee Springs basin (ISB) (Figure 1). This budget is based on information from direct measurements of N species in rainfall, ground water and spring waters, along with estimates of N loading to ground water from fertilizers, septic tanks, dry deposition, animal wastes, and the land application of wastewater and wastewater solids. Also, data on N-isotope composition and spring water ages are included to provide additional information on nitrate sources and ground-water flow pathways in the springs basin. Furthermore, geographical-system based techniques are used to estimate the spatial loading of N to ground water and assess areas most vulnerable to contamination within the basin.

DESCRIPTION OF ICHETUCKNEE SPRINGS BASIN

The 960-km^2 ISB lies within two distinct physiographic regions: the Northern Highlands and Gulf Coastal Lowlands (Figure 1). The Northern Highlands are characterized by relatively impermeable clay-rich sediments and numerous lakes and wetlands (Ceryak *et al.*, 1983; Crane, 1986). Soils developed in the Northern Highlands from phosphatic material (Scott, 1988) typically are well-drained to poorly drained sands (Houston *et al.*, 1965). In contrast, the Gulf Coastal Lowlands is a mature karst plain where very few lakes, wetlands, or surface water drainage occurs. Soils in the lowlands areas are moderately well-drained to excessively drained sands that are more than 75 cm thick (Houston *et al.*, 1965). Elevations typically are >50 m above sea level in the Northern Highlands and <30 m in the Gulf Coastal Lowlands. The transitional area between the highlands and coastal lowlands, referred to as the Cody Scarp, is characterized by sinking streams,

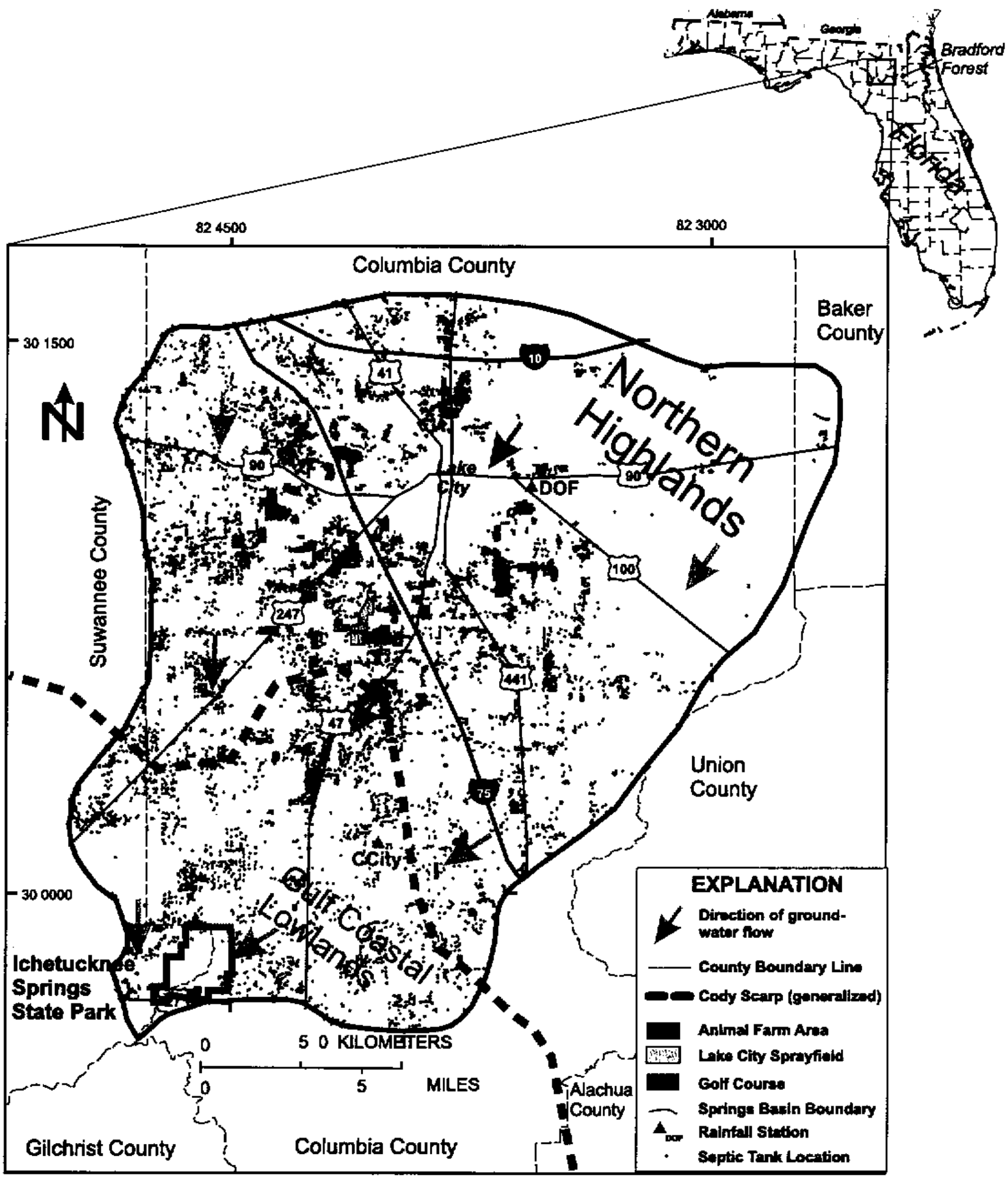

FIGURE 1. Map Showing Location of Cody Scarp, Septic Tanks, Golf Courses, and Land Application of Municipal Wastewater at Lake City Sprayfield in Ichetucknee Springs Basin.

numerous sinkholes, and sinkhole lakes (Upchurch, 2002). Surface runoff drains rapidly in the Cody Scarp mainly into sinkholes and other solution features that are directly connected to the Upper Floridan aquifer (UFA).

The springs basin also contains the Ichetucknee Trace (Figure 2), which is a dry river valley that extends about 11 km southwest from Cannon Creek Sink to the Ichetucknee River and springs. In the past, the Ichetucknee River flowed from Lake City, Florida, to the Santa Fe River. Cannon, Clay Hole, and Rose Creeks (Figure 2) were once tributaries of the Ichetucknee River, but now their flow is captured by sinkholes. During the past two centuries, sections of the Ichetucknee River likewise have been captured by sinkholes and streamwater now flows underground through caves. The present-day Ichetucknee River flows southwest from its headspring in Ichetucknee Springs State Park (ISSP) (Figure 2) about 7 km to its confluence with the Santa Fe River. During 2002-2005, the annual mean discharge from the Ichetucknee Head Spring and Blue Hole Spring

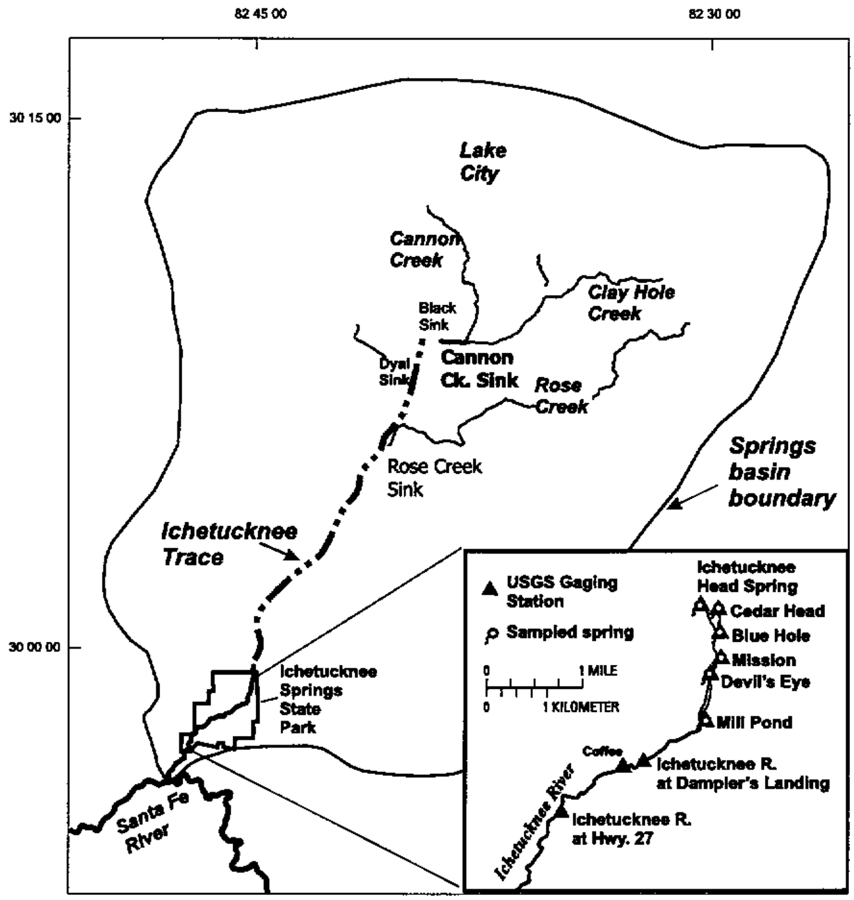

FIGURE 2. Map Showing Location of Sampled Springs, Ichetucknee Trace, and Disappearing Streams in the Ichetucknee Springs Basin.

(Figure 2) was 1.28 and 4.08 m^3/s, respectively, and make up more than 50% of the total annual mean discharge (9.24 m^3/s) for the Ichetucknee River (USGS, 2007). Continuous discharge measurements of several springs in ISSP (Head, Cedar Head, Blue Hole, Mission, Devil's Eye, Mill Pond, Coffee) and the Ichetucknee River at Dampier's Landing (Figure 2) have been made since February 2002. Discharge measurements are subject to an uncertainty range of ±10-15% depending on location within the springs basin and seasonal variations. Contributing factors to the uncertainty range include backwater effects following heavy rainfall events and varying amounts of submerged aquatic vegetation.

The ground-water contributing area for Ichetucknee springs (the ISB) was delineated from a detailed potentiometric surface map of the UFA, which was developed using 94 water-level measurements made by the Suwannee River Water Management District (SRWMD) in September 2003 (Sepulveda *et al.*, 2006). The ISB lies almost entirely within Columbia County in northern Florida, but a small portion along the west side of the Ichetucknee River and its headspring area, lies in adjacent Suwannee County, Florida, to the west. Ground-water flow is predominantly from north to south within the ISB (Figure 1). The UFA in the basin is characterized by very high transmissivity values that may range up to several million meters squared per day (m^2/day) (Bush and Johnston, 1988). These high values result from numerous voids created by the dissolution of limestone, and range in size from very small (few millimeters) to large caves (tens of meters).

Land use in the ISB is predominantly forest (52%), and other land-use types include agricultural (pasture, cropland, rangeland; 27%), water bodies and wetlands (9%), and urban (12%). Most of the urbanized land is in the vicinity of Lake City, which contains approximately 10,700 residents. In contrast, the northeastern parts of the ISB contain extensive forest and forested wetlands (Figure 3). In Columbia County, ground-water use in 2000 was principally for agriculture, and public and domestic water supply, which accounted for 42 and 53% of the total amount of ground water withdrawn (6.32×10^4 m^3/day), respectively (Marella, 2004).

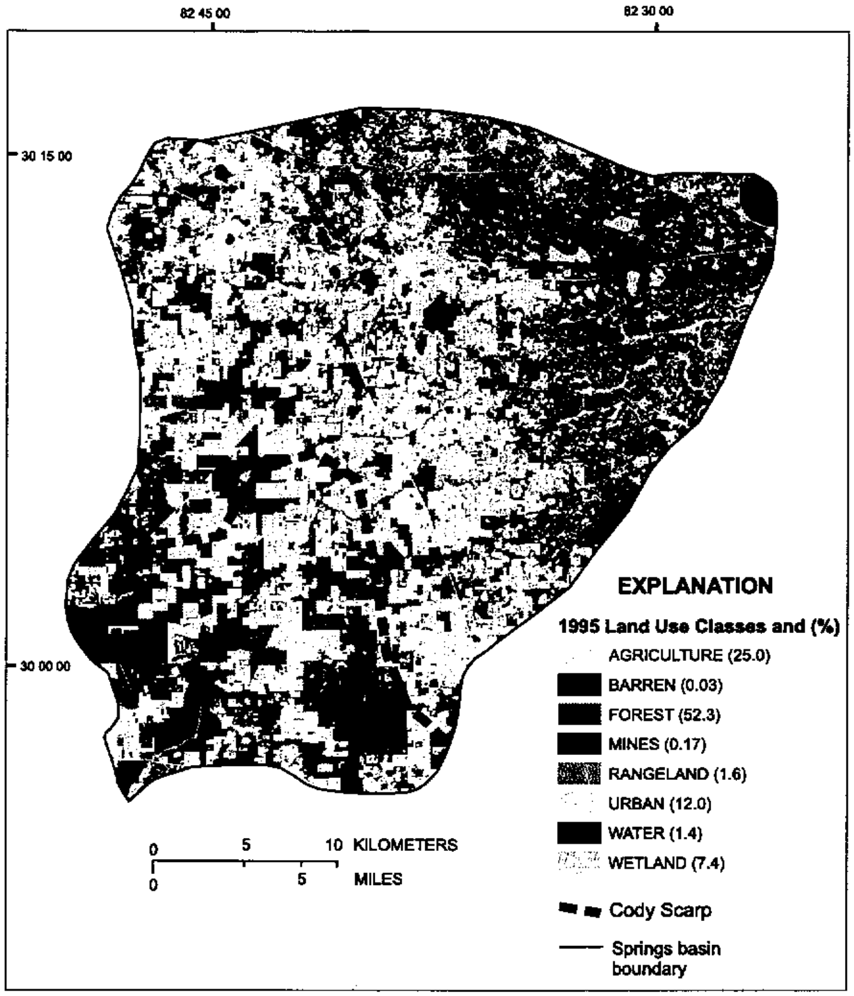

FIGURE 3. Map Showing Land Use (1995) in the Ichetucknee Springs Basin.

Climate in the ISB is subtropical (long, warm summers and mild winters). Rainfall amounts vary considerably from year to year in the basin, with a long-term annual average of 136.1 cm (1948-2006) at the National Weather Service station in Lake City. Estimates of ground-water recharge to the UFA in the ISB ranges from 45 to 80 cm/year where the aquifer is unconfined and 15-60 cm/year where the aquifer is poorly confined north of the Cody Scarp (Grubbs, 1998). Assuming that two-thirds of the basin is poorly confined and one-third is unconfined, it is estimated that 40 cm recharges the ground-water system annually. This represents about 30% of the average annual rainfall, which closely agrees with the recharge amount assuming a mean evapotranspiration rate of 67% (Bush and Johnston, 1988) for north-central Florida. The estimated recharge rate is 12.2 m^3/s for the entire springs basin (assuming steady-state conditions), which is similar to the mean annual discharge measured for six springs (12.1 m^3/s) in the State Park (USGS, 2007), suggesting steady-state conditions (minimal change in ground-water storage or deep ground-water flow that bypasses the springs that discharge water from the basin).

METHODS

The study included several approaches for estimating N inputs to ground water and vulnerability to contamination in the basin: (1) chemical analyses of rainfall, ground water, and spring waters; (2) geographical information systems (GIS) techniques to spatially evaluate N loading; and (3) N loading estimates from various sources.

Rainfall Chemistry

Two wet/dry atmospheric deposition collectors (DOF and CCity, Figure 1) were installed in the ISB (Figure 1) to quantify the contribution of N from atmospheric deposition over a 1-year period (March 2006-March 2007). One of the collectors (DOF) was co-located with a National Weather Service station in Lake City that has been in operation since July 1948. Both sites had a tipping bucket raingage to collect and measure rainfall and a data logger to record rainfall amounts every 15 min. Rainfall samples were collected biweekly from the wet bucket, and pH and specific conductance measurements were made on an aliquot from these samples. Samples from the two sites were analyzed for N species at the U.S. Geological Survey (USGS) National Water Quality Laboratory in Denver (Fishman and Friedman, 1989; Fishman, 1993). Protocols from the National Atmospheric Deposition Program were used for equipment set-up, collection, and processing of samples (http://nadp.sws.uiuc.edu/, accessed April 2008).

Spring-Water and Ground-Water Chemistry

Water samples were collected from six large springs that discharge ground water from the Ichetucknee basin (Figure 2). Specific conductance, pH, temperature, and dissolved oxygen were measured in the field using a multi-probe unit lowered directly into the spring vent. Standard field sampling protocols were used (USGS, 1997; Katz *et al.*, 1999). In addition to analyses for N species, water samples were analyzed for major ions, N and oxygen isotopes of nitrate, strontium isotopes, oxygen and hydrogen isotopes, tritium, and dissolved gases.

The stable isotope composition of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) of nitrate in water samples was analyzed by bacterial conversion of nitrate to nitrous oxide and subsequent measurement on a continuous flow isotope ratio mass spectrometer (Sigman *et al.*, 2001; Casciotti *et al.*, 2002; Coplen *et al.*, 2004). N-isotope ratios are reported using delta (δ) notation in per mil (‰) relative to N_2 in air (Mariotti, 1983). For samples with nitrate-N concentrations of at least 0.06 mg/l, the two-sigma uncertainty of N-isotopic results is 0.5‰, unless otherwise indicated. The uncertainty for nitrate samples with concentrations <0.06 mg/l as N is 1‰. Oxygen isotope ratios are reported relative to Vienna Standard Mean Ocean Water (VSMOW) reference water and normalized on a scale such that Standard Light Antarctic Precipitation (SLAP) reference water is −55.5‰ (Coplen, 1994). For water samples with nitrate-N concentrations of at least 0.06 mg/l, the 2-sigma uncertainty of oxygen isotopic results of nitrates is 1.0‰ unless otherwise indicated. The uncertainty is 2‰ for samples with nitrate-N concentrations <0.06 mg/l.

Estimates of N exported from the basin in spring waters were calculated by multiplying the N concentrations (sum of nitrate, ammonium, and organic N species) for each spring by its mean annual discharge (calendar year 2006), and summing the N loads from the six springs. Load estimates are subject to an uncertainty of about ±15% due to previously mentioned uncertainties in spring discharge measurements. Although spring waters were not sampled and analyzed for N species during variable flow conditions, the measured concentrations are expected to be representative of a range of flow conditions. A recent study found little variation (about ±10%) in nitrate-N concentrations between low- and high-flow conditions in 2005 for Blue Hole and Devil's Eye Springs (Katz and Griffin, 2008); however, another study in this area found larger temporal variations in nitrate concentrations in spring water (Martin and Gordon, 2000).

Nitrate-N concentrations in ground-water samples from 70 wells in the ISB were obtained from data collected mostly during 2000-2006 as part of a regional monitoring program by the SRWMD (Louis Mantini, SRWMD, 2007, written communication). Water samples were collected and analyzed using standard protocols (Florida Department of Environmental Protection, 2002). Well depths ranged from 8.8 to 62 m below land surface.

Geographical Information System Analyses

Land-use data (1995) were obtained from digitized maps from the SRWMD and were based on the Florida land-use and cover classification system. Spatial land-use data were intersected with the springs basin area that included county boundaries, GIRAS land use, topographic contours (1:24,000), hydrography, wetlands, lakes, census block groups, and 2004 digital orthophoto quadrangle quarters (DOQQs). Several areas in the springs basin were selected for field verification where land-use classification was suspected to be outdated or incorrect. Sewered areas in Lake City were digitized from maps obtained from the city of Lake City. Each household not in areas served by sewers (assumed to have a septic tank) in the springs basin was digitized from the 2004 DOQQs.

A model grid developed for the springs basin contained 155 rows and 157 columns of square cells (250 × 250 m). Nitrogen inputs were estimated for each cell based on land use and loading from associated N sources as described below. Topographic contours were used to prepare a coverage of sinkholes and closed depressions in the springs basin based on

1:24,000 scale maps from the SRWMD. A spatial assessment of vulnerability of the UFA to nitrate contamination was made by intersecting the sinkhole and closed depressions coverage with fertilizer application rates for each cell in the springs basin.

Estimates of Nitrogen Input to the Basin

Cropland Fertilizers. Recommended fertilizer application rates (Table 1) from the Florida Institute for Food and Agricultural Sciences (IFAS) (Kidder *et al.*, 1997; Obreza, 2004) were used to derive a weighted average of N for fertilizers applied to cropland in Columbia County (2002 Agriculture Census) and prorated for row crops grown in the springs basin (E. Toro, Columbia County Cooperative Extension Service, 2006, written communication). About 93% of the ISB area lies within Columbia County, therefore, it was assumed that the county estimates were applicable for the springs basin. Even though the springs basin area only occupies 44% of the total area of Columbia County, more than 50% of the agricultural activities in Columbia County are within the springs basin, and 66% of the cropland area in the county is contained within the springs basin.

Based on 1995 land use and Census of Agriculture data (2002), there were 49 row crop farms in the springs basin out of a total of 76 farms in Columbia County. Fertilizer application estimates also were made for other land-use activities including improved pasture and golf courses using recommended N application rates: (1) There are 533 farms in the springs basin with improved pasture classification out of a total of 688 farms in Columbia County. One fertilizer application per year was assumed for improved pasture at a rate of 52 kg N/ha (Sartain, 2000) and it was assumed that 50% of pasture land received fertilizers. (2) An average rate of 100 kg N/ha was assumed for the golf course in the springs basin, based on recommended applications of 24 kg/ha four times per year (Obreza, 2004). (3) For orchards and groves (blueberries, pecans, other fruit), the N fertilizer rate was 100 kg/ha (Obreza, 2004).

Fertilizers Applied to Lawns. Nitrogen loads from fertilizers applied to lawns in the basin were estimated from IFAS recommended application rate for turfgrass of 48 kg/ha (0.45 kg of fertilizer per 0.0093 ha) four times per year. It was assumed that N comprises about 20% of the applied fertilizer and the average yard size fertilized was 0.11 ha. There are an estimated 15,000 yards in the basin. However, it was assumed that only 50% of those received fertilizers, which also accounts for natural landscapes that may receive little or no fertilizers and manicured lawns that may receive high N fertilizer applications.

Fertilizers Applied to Pine Stands. Fertilizers (typically diammonium phosphate) are applied to

TABLE 1. Recommended Nitrogen Application Rates for Fertilizing Various Crops, Turfgrass, Pine Stands, and Improved Pasture; and Application Rates Used in Mass-Balance Calculations.

Land Use	Recommended N Application Rate (kg/ha/year)	N Application Rate Used in Mass Balance Calculations (kg/ha/year)	Area Receiving Fertilizers (ha)	N Input to Surface (kg/year)	Reference
Golf courses	97-390	100	120	12,000	Obreza (2004)
Improved pasture	0-202	52	10,100	525,200	Assumes 50% pasture areas fertilized (Obreza, 2004)
Row crops (weighted average for Columbia Co.)		120	1,275	153,000	
Corn (nonirrigated and irrigated)	168-235				Kidder *et al.* (1997)
Rye, wheat	78				Kidder *et al.* (1997)
Tobacco	90				Kidder *et al.* (1997)
Tomatoes, potatoes, peppers	224				Hochmuth and Hanlon (2000)
Beans	67-112				Hochmuth and Hanlon (2000)
Watermelons	168				Hochmuth and Hanlon (2000)
Fruit orchards	90-112	100	10	1,000	Obreza (2004)
Blueberries	67-134	100	20	1,980	University of Arkansas (2004)
Other groves	90-112	100	5	496	Obreza (2004)
Pecans	90-112	100	138	13,800	Obreza (2004)
Established pine stands	24-32	21	12,365	259,665	Assumes 50% stands fertilized (Jokela and Long, 2000)
Young pine stands	45-56	7	945	6,615	Assumes 50% stands fertilized (Jokela and Long, 2000)

Note: kg/ha/year, kilograms per hectares per year; N, nitrogen.

young and established pine stands in the basin; however, these amounts/rates can be highly variable (Table 1). Forested areas in the basin that contain pine stands represent about 30% of the total area of the springs basin, and the amount of N (and phosphorus) applied to these stands could be significant. For young stands in moderately well-drained soils, recommended N application rates are 45-56 kg/ha for N (Jokela and Long, 2000). Young pine stands are fertilized at planting and generally do not receive fertilizers for about eight years, so the assumed annual rate is 7 kg N/ha. For established stands, higher growth responses were noted with application rates of 168-224 kg N/ha (Jokela and Long, 2000) over a growing period of 8-10 years, so an annual application rate of 21 kg/ha was assumed for these types of stands in the basin. Although most of the pine stands are in the northeastern part of the springs basin, there are several pine stands within a 16-km radius of the springs (Figure 3). As a first approximation of the amount of N applied to pine stands, it was assumed that fertilizers were applied to only 50% of the young stands (total 1,890 ha) and to 50% of the established pine stands (total 24,700 ha) (Table 3). The area of young pine stands was determined from differences in forested areas using land use coverages from 1977 and 1995.

Septic Tanks. A geographical coverage of sewered areas in Lake City was overlain on a map of residential land-use classifications (low-, medium-, and high-density). Most high-density residential land use was in the sewered areas of Lake City, but not all of the medium density land use was sewered. There were an estimated 14,090 households with septic tanks (Figure 1), which is about 67% of the estimated county total of 21,000 households. The average number of household occupants (2.56) was multiplied by an N loading rate of 4.24 kg/person per year (Maizel *et al.*, 1997) to obtain 10.9 kg N per household per year. Similar estimates of per capita N loading from septic systems range from 4.1 to 6.4 kg/year (Almasri and Kaluarachchi, 2004) or 10.5-16.4 kg N/year per household assuming 2.56 persons per household.

Land Application of Treated Municipal Wastewater and Biosolids. Nitrogen inputs to the land surface from application of treated municipal water at a sprayfield in Lake City (Figure 1) were estimated using an average total N concentration for the sprayfield effluent (8 mg/l) and an average volume of treated wastewater (10,600 m^3/day). Nitrogen loading to the land surface (236 ha) from biosolids from the wastewater treatment plant was estimated by multiplying the amount of applied biosolids (443 metric tons/year) times its N content (3%).

Animal Wastes. Nitrogen inputs from animal wastes in the basin were calculated from the N content in manure and information on animal populations. Animal populations in the basin were prorated from Columbia County data (2002 Florida Agriculture Census) based on the ratio of pasture area in the basin relative to that in the county (0.66). Estimated numbers of animals in the springs basins are 12,754 cows, 438 hogs, 198,480 chickens, 626 horses, 120 sheep and lambs, and 880 goats. Nitrogen content of manure (kg/year) produced by the various animals was: cows, 50; hogs, 7.7; chickens, 0.3; horses, 43; sheep and lambs, 5.8, and goats, 5.8 (Goolsby *et al.*, 1999; Quynh *et al.*, 2005; Ruddy *et al.*, 2006).

RESULTS

Nitrogen Loading to Ground Water From Various Sources and Uncertainty Estimates

Nitrogen loading to ground water (N_{gw}) in the basin was estimated from N inputs to the land surface or near land surface for each source (i) and N losses (sinks) as in Equation (1):

$$N_{gw} = \sum (N_{\text{inputs from sources(i)}} - N_{\text{losses for sources(i)}}), \qquad (1)$$

where sources (i) include atmospheric deposition, fertilizers, animal wastes, and human wastewater and N losses for each source (i) include processes such as uptake by vegetation and soils, harvesting (removal from basin), and denitrification. Nitrogen loss estimates associated with each source are subject to considerable uncertainty due to the lack of direct measurements of N uptake by soils and vegetation, mineralization of organic N, volatilization losses, and denitrification. As a result, uncertainty in N loading estimates to ground water from each source were incorporated using minimum and maximum N leaching estimates based on studies in the basin and from relevant literature.

Atmospheric Deposition. Generally, rainfall amounts were similar at both sites for the biweekly samples during the study (March 2, 2006-March 13, 2007) (Table 2 and Figure 4); however, there were two sampling periods when the amount of rainfall was at least 4-6 cm higher at the CCity site than the DOF site. No rain-water samples were collected at the DOF site during July 2006 due to equipment failure. At both sites, the nitrate-N concentrations were inversely related to the amount of rainfall. Higher

TABLE 2. Physical Properties, and Nitrogen Species Concentrations and Loading for Rain Water Collected at the CCity and DOF Sites.

Sample Begin Date	Sample End Date	Comment	Specific Conductance	pH (standard units)	Ammonia (mg/l as nitrogen)	Nitrite Plus Nitrate (mg/l as nitrogen)	Rainfall (cm)	Nitrate-N (kg)	Total N (kg)	N (kg/ha)	Ammonium-N, (kg/ha)	Nitrate-N (kg/ha)
CCity Rainfall Collection Site												
3/2/2006	3/28/2006		20	5.0	0.26	0.42	0.81	3,390	5,489	0.055	0.021	0.034
3/28/2006	4/11/2006		8	5.1	0.14	0.11	1.27	1,387	3,153	0.032	0.018	0.014
4/11/2006	4/25/2006		7	6.1	0.32	0.30	0.91	2,724	5,631	0.057	0.029	0.027
4/25/2006	5/9/2006		10	4.8	0.15	0.20	2.31	4,591	8,035	0.081	0.035	0.046
5/9/2006	5/23/2006		10	5.1	0.70	0.33	0.94	3,080	9,614	0.097	0.066	0.031
5/23/2006	6/6/2006		15	6.2	0.331	0.44	0.84	3,663	6,418	0.065	0.028	0.037
6/6/2006	6/20/2006		4	7.3	0.025	0.03	10.95	3,588	6,306	0.063	0.027	0.036
6/20/2006	7/5/2006		11	5.2	0.129	0.15	6.81	10,141	18,862	0.190	0.088	0.102
7/5/2006	7/18/2006		12	5.2	0.175	0.33	1.52	4,995	7,644	0.077	0.027	0.050
7/18/2006	8/1/2006		13	5.1	0.065	0.28	6.22	17,305	21,322	0.215	0.040	0.174
8/1/2006	8/15/2006		13	5.0	0.057	0.29	2.82	8,120	9,716	0.098	0.016	0.082
8/15/2006	8/29/2006		12	5.1	0.088	0.15	10.52	15,666	24,856	0.250	0.093	0.158
8/29/2006	9/12/2006		12	5.0	0.046	0.20	3.84	7,618	9,371	0.094	0.018	0.077
8/29/2006	9/12/2006	R	12	5.0	0.048	0.20	3.84	7,618				
9/12/2006	9/26/2006		12	5.2	0.109	0.19	4.17	7,861	12,370	0.125	0.045	0.079
9/12/2006	9/12/2006	B	NM	NM	<0.01	<0.06						
9/26/2006	11/7/2006		4	7.9	0.002	0.02	4.11	613	695	0.007	0.001	0.006
11/7/2006	11/21/2006		21	6.2	E0.04	0.12	2.44	2,906	3,875	0.039	0.010	0.029
11/21/2006	12/5/2006		39	7.1	0.056	0.25	1.14	2,838	3,474	0.035	0.006	0.029
12/5/2006	1/3/2007		7	7.7	E0.018	0.07	17.91	12,449	15,650	0.158	0.032	0.125
1/3/2007	1/17/2007		9	7.6	E0.018	0.07	2.31	1,607	2,020	0.020	0.004	0.016
1/17/2007	1/30/2007		15	7.5	0.096	0.15	3.81	5,676	9,308	0.094	0.037	0.057
1/30/2007	2/13/2007		8	7.0	0.092	0.08	4.88	3,875	8,331	0.084	0.045	0.039
2/13/2007	2/27/2007		14	7.3	0.097	0.19	0.76	1,438	2,172	0.022	0.007	0.014
2/27/2007	3/13/2007		10	S7.1	0.074	0.11	5.97	6,521	10,908	0.110	0.044	0.066
DOF Rainfall Collection Site												
3/2/2006	3/28/2006		27	5.3	0.45	0.53	1.19	6,284	11,619	0.117	0.054	0.063
3/28/2006	4/11/2006		11	6.8	0.14	0.09	1.32	1,181	3,017	0.030	0.018	0.012
4/11/2006	4/25/2006		12	7.0	0.27	0.24	1.17	2,785	5,918	0.060	0.032	0.028
4/25/2006	5/9/2006		10	4.8	0.22	0.18	4.47	7,992	17,759	0.179	0.098	0.080
5/9/2006	5/23/2006		10	5.6	0.41	0.4	1.32	5,247	10,625	0.107	0.054	0.053
5/23/2006	6/6/2006		18	5.0	<0.01	0.26	1.40	3,607	3,746	0.038	0.001	0.036
6/6/2006	6/20/2006		17	7.5	0.017	0.002	11.63	231	2,195	0.022	0.020	0.002
6/20/2006	7/5/2006		11	7.3	0.135	0.17	9.07	15,310	27,468	0.277	0.122	0.154
8/1/2006	8/15/2006		45	4.1	0.037	1.0	0.48	4,793	4,970	0.050	0.002	0.048
8/15/2006	8/29/2006		21	7.3	0.011	0.19	4.80	9,059	9,583	0.096	0.005	0.091
8/29/2006	9/12/2006		10	4.7	E0.009	0.14	7.80	10,842	11,539	0.116	0.007	0.109
8/29/2006	9/12/2006	R	10	4.7	E0.009	0.14	7.80	10,842	11,539			
9/12/2006	9/26/2006		10	5.0	0.034	0.15	3.20	4,768	5,848	0.059	0.011	0.048
9/12/2006	9/12/2006	B	NM	NM	<0.01	<0.06						
9/26/2006	11/7/2006		10	7.5	E0.007	0.06	3.23	1,922	2,146	0.022	0.002	0.019
11/7/2006	11/21/2006		16	6.8	0.097	0.12	2.97	3,542	6,405	0.064	0.029	0.036
11/21/2006	12/5/2006		39	4.8	0.071	0.448	0.43	1,921	2,226	0.022	0.003	0.019
12/5/2006	1/3/2007		6.6	5.1	E0.018	0.07	13.87	9,641	12,121	0.122	0.025	0.097

TABLE 2. (Continued)

Sample Begin Date	Sample End Date	Comment	Specific Conductance	pH (standard units)	Ammonia (mg/l as nitrogen)	Nitrite Plus Nitrate (mg/l as nitrogen)	Rainfall (cm)	Nitrate-N (kg)	Total N (kg)	N (kg/ha)	Ammonium-N, (kg/ha)	Nitrate-N (kg/ha)
1/3/2007	1/17/2007		15	5.1	0.021	0.12	3.02	3,602	4,233	0.043	0.006	0.036
1/17/2007	1/30/2007		17	6.2	0.114	0.2	4.29	8,526	13,387	0.135	0.049	0.086
1/30/2007	2/13/2007		8	5.2	0.094	0.08	4.11	3,269	7,111	0.072	0.039	0.033
2/13/2007	3/13/2007		8	5.0	0.095	0.14	4.93	6,851	11,501	0.116	0.047	0.069

Notes: B, blank water sample; blank cell, not analyzed due to an insufficient amount of rain water; cm, centimeters; E, measurable concentration below the laboratory method reporting level; ha, hectares; kg, kilograms; mg/l, milligrams per liter; N, nitrogen; NM, not measured; R, replicate sample.
Specific conductance in microsiemens per centimeter at 25°C.
Dates are mm/dd/yyyy notation.

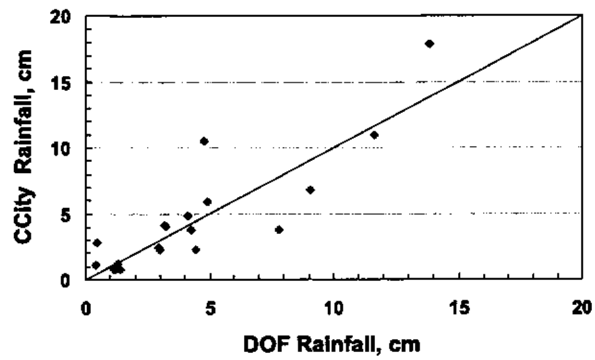

FIGURE 4. Comparison of Rainfall Amounts at the CCity and DOF Stations (see Figure 1 for locations).

nitrate-N concentrations (0.4-1.0 mg/l) generally were observed in samples with 1.2 cm or less rainfall.

Biweekly nitrate-N inputs to the basin from rainfall are similar for the two sites (Table 2). However, during the study period, rainfall N deposition rates were much higher (1.6 times) at the CCity site than at a National Atmospheric Deposition Station in nearby rural Bradford County (Figure 5) (Bradford Forest site, Figure 1), which was used to estimate N loads from rainfall in previous studies (Katz *et al.*, 1999). Factors that may account for the higher deposition rates in the ISB include higher rainfall amounts, and local atmospheric inputs of N from volatilization of ammonia from fertilizers and animal wastes, and N from combustion of fossil fuels.

Nitrogen inputs from dryfall (N in particles and aerosols that settle out of the atmosphere during dry periods) was estimated by multiplying the N load in rainfall by a dry-deposition enrichment factor. Using

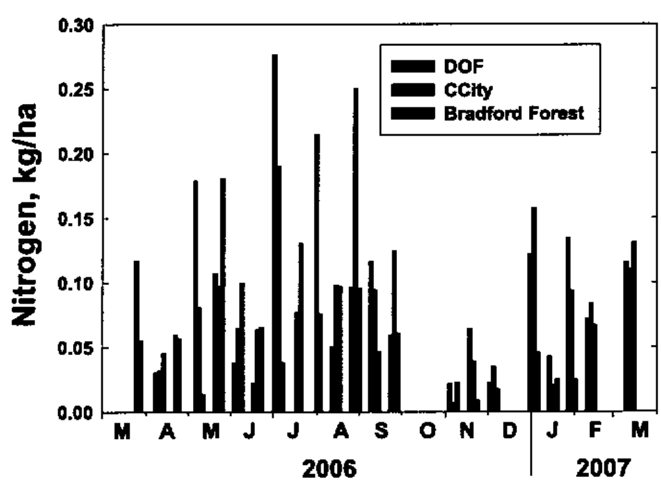

FIGURE 5. Nitrogen Deposition in Rain Water Collected at the Two Rainfall Monitoring Sites and the National Atmospheric Deposition Program Station in Bradford Forest in Bradford County, Florida.

TABLE 3. Estimates of Nitrogen (N) Inputs to the Land Surface, Nitrogen Loading to Ground Water, and Nitrogen Export From Spring Waters in the Ichetucknee Springs Basin.

	Nitrogen Input to Surface (kg/year)	Minimum Fraction Leaching to Ground Water (%)	Minimum Nitrogen Load to Ground Water (kg/year)	Maximum Fraction Leaching to Ground Water (%)	Maximum Nitrogen Load to Ground Water (kg/year)	Based on Minimum Leaching Rate (maximum N losses) (%)	Based on Maximum Leaching Rate (minimum N losses) (%)
Source							
Atmospheric deposition	402,230	0.05	20,112	0.3	120,669	7.7	9.0
Fertilized cropland	707,470	0.10	70,747	0.5	353,735	27.0	26.3
Fertilized yards	372,770	0.10	37,277	0.5	186,385	14.3	13.9
Fertilized pine stands	266,280	0.10	26,628	0.5	133,140	10.2	9.9
Sprayfield	30,980	0.10	3,098	0.5	15,490	1.2	1.2
Biosolids	13,250	0.20	2,650	0.3	3,975	1.0	0.3
Animal wastes	706,340	0.10	70,634	0.6	423,804	27.0	31.5
Septic tanks	152,040	0.20	30,408	0.7	106,428	11.6	7.9
Total	2,651,360		267,554		1,343,626		
N export in spring waters			266,260 ±39,900		266,260 ±39,900		

Notes: %, percent; kg/year; kilograms per year; N, nitrogen.

a mean total dry-deposition flux of N (0.96 times the wet-deposition flux) for northern Florida (Baker, 1991), yields a combined N atmospheric deposition load of 402,230 kg for the 12-month period (Table 3). Due to the below normal amount of rainfall during the study period (97.3 cm), N loading likely is about 30% lower than what would be calculated for an annual average rainfall of 136 cm.

Nitrogen retention by soils and vegetation from atmospheric wet and dry deposition in forested and mixed land-use catchments can vary widely. Dewalle *et al.* (2005) found that the retention efficiency (N uptake rate) of five Applachian forested watersheds ranged from 63 to 96%. Another study of coniferous forests found that at over 30 sites receiving up to 14 kg/ha/year of total N deposition, N leaching was found to be practically zero (Nilsson *et al.*, 1998). Also, based on a background N concentration of 0.05-0.1 mg/l for ground water in undeveloped areas of the basin (Maddox *et al.*, 1992), and rainfall N concentrations of 0.5-1 mg/l, only about 10% of rainfall N leaches to ground water. From these N loss estimates, atmospheric deposition would contribute 20,110 to 120,700 kg N/year to ground water in the springs basin (Table 3).

Fertilizers. Nitrogen inputs to the land surface from fertilizers applied to cropland, improved pastures, and golf course turf totaled 707,470 kg/year (Table 3). Nitrogen leaching from fertilizers is related to the specific fertilizer management practices at a particular farm, soil texture, recharge (and irrigation), and application rates (Di and Cameron, 2002; Green *et al.*, 2008), but high temporal and spatial variability are typical throughout the unsaturated zone (Onsoy *et al.*, 2005). Losses of N from volatilization of ammonia in fertilizers can vary considerably depending upon the specific fertilizer formulation and management practices (Canter, 1997). Estimated N inputs to the land surface from cropland fertilizers were based on the assumption one crop per year; however, this estimate likely is conservative as some of the farms grow two crops in any given year. Studies of ground water beneath heavily fertilized well-drained fields indicate nitrate recharge (leaching) rates that are 10-50% of fertilizer N application rates (Böhlke and Denver, 1995; Lauver and Baker, 2000; Böhlke, 2002). Based on this range, cropland fertilizers would contribute between 70,750 and 354,000 kg N/year to ground water. Again, based on the aforementioned range of nitrate recharge, lawn fertilizers would contribute between 37,280 and 186,400 kg/year to ground water in the basin (Table 3). Estimated N loading from fertilizers applied to pine stands was 266,000 kg/year, and using the aforementioned leaching rates, yields about 26,600 to 133,00 kg/year to ground water.

Human and Animal Wastes. Estimated N loading from septic systems totaled 152,000 kg/year. Studies have shown a wide range of N removal from 30% (University of Wisconsin, 1978) to 80% (Gerritse *et al.*, 1995) due to denitrification, soil uptake, and vegetative uptake from drainfields (Harris, 1995).

Anderson and Otis (2000) estimate that 50-90% of N released from septic tanks reaches the water table. Based on these estimates, septic tank effluent contributes between 30,400 and 106,400 kg/year to ground water (Table 3).

Nitrogen input from sprayfield irrigation of treated municipal wastewater totaled 31,000 kg/year. Nitrogen losses from the land application of treated effluent vary from about 50-100% depending on soil type (Barton *et al.*, 2005). Approximately 75% removal of total N was found during a study of the Lake City sprayfield (Katz and Griffin, 2008), which is similar to the 70-80% N removal by plant uptake and harvesting for a sprayfield study in Pennsylvania (Schreffler *et al.*, 2005). Based on these studies, sprayfield irrigation contributes an estimated 3,100 to 15,500 kg/year to ground water in the basin. Nitrogen inputs to the land surface from biosolids applications are 13,250 kg/year. Studies have found that 20-30% N is leached from land application of biosolids due to volatilization, and soil and plant uptake (Lauver and Baker, 2000), although a considerable range in N leaching can result from biosolids type and application rates, soil characteristics, and plant uptake (USEPA, 2000; Currie *et al.*, 2003; Bell *et al.*, 2006; Correa *et al.*, 2006). Based on these leaching estimates, the land application of biosolids would contribute between 2,700 to 4,000 kg N/year to ground water.

Estimated N inputs to the land surface from animal wastes totaled 706,340 kg/year (Table 3). Leaching of N from animal wastes also can vary considerably depending upon wet or dry storage and land application methods, animal-waste type, and volatilization losses that vary with temperature, soil pH, soil moisture, and other processes (Kay and Hammond, 1985; Van Horn *et al.*, 1991; Vest and Merka, 1994). Nitrogen losses from animal wastes through volatilization can range from 50 to 95%, depending on storage, handling, and field application methods (Lauer *et al.*, 1976; Hoff *et al.*, 1981; Burkhart and James, 1999). Also, the actual number of animals in the springs basin can vary annually. For example, during 1990-2007, the number of beef cows in Columbia County ranged from 9,000 in 1992 to 13,000 in 1998, 2001, and 2002 (Florida Agricultural Census). Based on N leaching rates of 10-50%, animal wastes would contribute between 70,600 and 423,800 kg/year to ground water in the basin.

Nitrate in Ground Water, and Nitrate and Nitrogen Isotopes in Spring Waters

Nitrate-N (nitrite-N plus nitrate-N) concentrations in ground water ranged from <0.01 to 6.1 mg/l, with a median concentration of 0.41 mg/l. Water from 11 wells had nitrate-N concentrations >1.0 mg/l. There was no apparent relation between nitrate concentration and well depth. However, there was a significant correlation between nitrate and potassium concentrations ($p < 0.05$), which indicates fertilizers likely are a dominant source of nitrate in ground water.

Nitrate-N concentrations in spring waters ranged from 0.52 to 0.87 mg/l (Table 4). Concentrations of ammonium-N and organic N were below laboratory method reporting levels (0.02 and 0.1 mg/l, respectively). N-isotope ratios were low, ranging from 3.3 to 6.3‰ that are consistent with values observed elsewhere for ground water nitrate recharged beneath cultivated land receiving artificial fertilizers (Kendall and Aravena, 2000). Higher N-isotope ratios ($\delta^{15}N$-NO_3 = 6.1-6.3‰) were found in Mission and Mill Pond Springs, which also contained lower concentrations of nitrate-N and dissolved oxygen (0.3-0.6 mg/l) than the four other spring waters. Some denitrification could account for the lower nitrate concentration and slightly higher N-isotope ratios in these two spring waters; however, no excess N_2 gas concentrations were found and low organic carbon concentrations were similar to other sampled spring waters.

Differences in nitrate, major-ion, and isotopic composition of the six spring waters (Table 4) reflect variable amounts of recharge through confining material in the ground-water contributing area for each spring. Mill Pond Spring has the highest sulfate, fluoride, magnesium, silica, boron, and phosphate concentrations (Table 4), indicating that recharge likely occurs through low permeable Hawthorn clay material (Lawrence and Upchurch, 1982; Katz, 2004). Source areas for Mission and Devil's Eye Springs also reflect relatively deep flow of water through the UFA, but elevated nitrate concentrations indicate that mixing of water from different water-quality domains likely is occurring near these springs (Champion and Upchurch, 2006).

DISCUSSION

Comparison of Nitrogen Loading to Ground Water and Output Loads in Spring Waters

Estimated total N loads to ground water from all sources range from 261,500 to 1,344,000 kg/year (Table 3). Based on minimum and maximum estimates of N leaching to ground water for the different sources, fertilizers applied to cropland, yards, and pine stands contributed the highest percentage of total N inputs to ground water (50-52%) in the basin

TABLE 4. Physical Properties and Concentrations of Major Dissolved Constituents, Isotopes, and Selected Trace Elements in Water Samples From Springs in Ichetucknee Springs State Park.

Spring Name	Sampling Date	Time	Mean Annual Discharge (March 2006-February 2007) (m^3/s)	Temperature, Water (°C)	Specific Conductance (microsiemens per centimeter)	Dissolved Oxygen (mg/l)	pH (standard units)	Ammonia, as Nitrogen	Ammonia Plus Organic Nitrogen, as Nitrogen	Nitrite Plus Nitrate, as Nitrogen	Orthophosphate, as Phosphorous	Organic Carbon
Ichetucknee Head	1/30/2007	1430	1.85	21.7	320	4.0	8.40	<0.02	<0.10	0.83	0.022	1.2
Cedar Head	1/30/2007	1130	0.25	21.5	314	3.9	8.20	<0.02	E0.07	0.87	0.03	1.8
Blue Hole	1/30/2007	1300	4.05	21.7	294	2.0	8.30	<0.02	<0.10	0.76	0.048	1.3
Devil's Eye	1/31/2007	1000	1.36	21.8	326	0.8	7.95	<0.02	E0.05	0.61	0.059	1.1
Mill Pond	1/30/2007	1630	0.82	21.8	338	0.3	8.40	<0.02	<0.10	0.52	0.061	1.1
Mission	1/31/2007	1200	2.34	21.7	311	0.6	7.50	<0.02	<0.10	0.59	0.06	1.2
Mission-R	1/31/2007	1230		21.7	311	0.6	7.50	<0.02	<0.10	0.59	0.06	1.2

Spring Name	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Fluoride	Silica	Bicarbonate (HCO3)	Delta Nitrogen-15 of Nitrate	Delta Oxygen-18 of Nitrate
Ichetucknee Head	57	6.1	2.6	0.16	4.3	8.2	0.11	7.1	193	3.4	4.6
Cedar Head	54	5.6	2.6	0.21	4.5	5.7	0.14	7.9	190	3.3	4.8
Blue Hole	52	5.0	3.1	0.37	4.9	4.5	0.13	9.0	178	4.1	5.7
Devil's Eye	50	7.1	4.5	0.55	6.3	9.6	0.18	12	182	5.8	7.2
Mill Pond	52	8.8	5.1	0.58	6.9	21	0.23	13	184	6.3	8.3
Mission	50	5.8	4.0	0.51	5.8	5.6	0.16	11	178	6.1	8.0
Mission-R	50	5.8	4.0	0.45	5.9	5.6	0.17	11	178	6.1	7.7

Notes: °C, degrees Celsius; E, estimated value below method reporting level; mg/l, milligrams per liter; R, replicate sample.
All concentrations are in milligrams per liter unless otherwise noted.
All isotopic compositions are expressed as delta values in per mil relative to standards.
Dates are mm/dd/yyyy notation.

(Table 3). Similar ground-water N loading percentages for fertilizers (54%) were found for the larger Wekiva Springs basin (1,680 km^2) in central Florida (MACTEC, 2007). Other sources contributed the following percentages of the total estimated N load to ground water: animal wastes (27-32%), septic tanks (8-12%), atmospheric deposition (8-9%), and land application of treated wastewater and biosolids (1.5-2.2%). The dominant N loading to ground water from fertilizers (50-52%) is consistent with N-isotope data for spring waters, elevated potassium concentrations in ground water, and information from previous studies. Nitrogen inputs from fertilizers were the dominant source of N inputs to the land surface for several counties in the lower Suwannee River basin (Katz *et al.*, 1999). Fertilizer sales peaked in the late 1970s for Columbia County, but sales for Columbia County and other adjacent counties also increased substantially during 1993-1997 (Katz *et al.*, 1999).

Total N loads to ground water, assuming minimal leaching rates (10-20%), agreed closely with the amount of N exported from the basin in spring waters (266,300 ± 39,900 kg/year), based on the sum of N loads from six springs (Cedar Head Spring, Ichetucknee Head Spring, Mission Spring, Mill Pond Spring, Devil's Eye Spring, and Blue Hole Spring) (Figure 2). Minimal leaching losses (10-20%) in this study are similar to those estimated for the Wekiva basin (18%) and for agricultural applications in Florida (5-30%) (Bottcher and Rhue, 2000). Nitrogen export from the springs basin corresponds to 2.8 kg N/ha, which is considerably lower than N export from other karst basins with higher percentages of agricultural land use: Illinois (27 kg N/ha/year) (Panno and Kelly, 2004), Kentucky (6-23 kg N/ha/year) (Currens, 1999), and Arkansas (5.02 kg/ha/year) (Peterson *et al.*, 2002).

Estimates of N loading to ground water in excess of that exported from the basin in spring waters could result from overestimates of N inputs and/or underestimates of N losses. Although other studies have attributed excess N inputs to overestimating fertilizer or other inputs, or by underestimating loss processes (Quynh *et al.*, 2005; MACTEC, 2007), these two possibilities are unlikely in this basin. Conservative estimates of fertilizer inputs were based on recommended application rates (which typically are lower than actual application rates), and on one crop grown per year. Other factors that could account for excess N inputs relative to outputs are the lag time between inputs to the surface and recharge (loading) to the water table, historical variations in annual N inputs, and ground-water residence time. Previous age-dating studies of spring waters in northern Florida have found that spring waters (Ichetucknee Head Spring, Mission Springs, and Blue Hole Spring) likely contain mixtures of waters recharged during the past 10-30 years with those that were recharged more than 50 years ago (Katz, 2004). Thus, estimated N inputs to ground water from recent agricultural land-use information may not account for N loading variations over the past 40-50 years. Fertilizer sales peaked in the late 1970s in Columbia County, whereas estimated loading from other N sources was considerably lower and remained steady over the past four decades (Katz *et al.*, 1999). Spring water nitrate concentrations represent a combination of rapid influx from the surface along large openings and much slower leaching from matrix flow; although nitrate concentrations can vary temporally depending on the relative proportions of conduit and matrix flow (Martin and Gordon, 2000). Iqbal and Krothe (1995) found that the matrix flow played an important role in nitrate leaching over long time periods, and this leaching resulted in alternate layers of nitrate in the unsaturated zone derived from two sources, inorganic fertilizer and animal wastes.

Loss of N due to denitrification likely is not a dominant process for N removal in the springs basin. Soils in the basin generally contain very little organic matter, and ground water typically is oxic and contains little organic carbon needed for denitrification. Also, dissolved gas data for spring waters are consistent with atmospheric equilibration during recharge with little or no measured excess N, which would indicate denitrification. However, it cannot be ruled out that denitrification may have occurred sometime in the past.

Nitrogen Storage in Soils and Unsaturated Zone

Losses of N below the root zone (storage in the unsaturated zone) may account for low N leaching rates from fertilizers to ground water in the springs basin. A study in nearby Suwannee County, just west of the ISB, found that significant levels of nitrate and ammonium from fertilizers leach below the root zone and are retained in the subsurface beneath cropland fields. During 2000-2006, median nitrate-N concentrations in soil at a 2-m depth were 71 kg/ha/year and 69 kg/ha/year beneath two fields that received an average of 297 kg N/ha/year and 249 kg N/ha/year, respectively (Graetz *et al.*, 2007). Another study at the nearby Suwannee Valley Research and Education Center in Live Oak, Florida, during 2002-2006, ammonium-N and nitrate-N median levels in soils (2-m depth) were 28 and 85 kg/ha/year beneath fields where bermuda grass forage was fertilized at an average rate of 300 kg/ha/year (average rainfall during the study was 133.5 cm). High accumulation of soil ammonium was surprising given that the nitrification would be expected to convert most of the ammonium to nitrate. These two studies showed that significant amounts of ammonium-N (28%) and to a lesser extent nitrate-N (10%) can build up annually in the soil and unsaturated zone beneath the root zone in agricultural areas.

Several long-term studies also have found that substantial amounts of soil N can build up over long periods of time beneath fertilized cropland areas (Almasri and Kaluarachchi, 2004). Although N storage in the unsaturated zone is related to fertilizer type (e.g., relative amounts of N, P, K), soil characteristics, crop type, and other processes, long-term studies have found that nitrate-N accumulation was highest in the 1.8-2.1 m soil depth, which indicated that N leaching reached deeper soil layers after annual application of chemical fertilizers for 23 years (Yang *et al.*, 2006). In another study, Steinheimer and Scoggin (1998) found that 31% of applied N is being stored in the soil or gradually depleted by soil microorganisms, based on findings from a 23-year watershed study. Nitrogen storage was inversely related to cumulative N uptake by crops in a 22-year study (Benbi and Biswas, 1997).

Even if maximum N leaching rates from fertilizers (50%) are assumed, as much as 26 kg N/ha could be stored in the unsaturated zone in the basin, which is within the range of N found in soils beneath row crops and improved pasture found in the Suwannee County study (Graetz *et al.*, 2007). Studies in other karst basins also have reported high nitrate leaching rates (Liu *et al.*, 1997; Peterson *et al.*, 2002) with storage likely in the unsaturated zone. Annual nitrate-N losses as high as 27 kg N/ha have been reported for karst basins in Illinois (Panno and Kelly, 2004). Nitrate-N export for 1992-93 were 17.7 kg/ha, which was only about 12% of nitrate-N applied to crops in a spring basin in Kentucky (Currens, 1999). This low mass flux of nitrate-N observed at Pleasant Grove Spring was attributed to storage in slow-flow zones of the aquifer, which was supported by concentration trends of other chemical constituents (Currens, 1999).

Assessing Vulnerability to Nitrate Contamination from Fertilizers in the Springs Basin

Spatial patterns of N loading to the springs basin provide information about vulnerability of spring waters to proximal sources of contamination. As fertilizer inputs are the dominant source of nitrate to ground water, N loading from fertilizer application to cropland are shown in Figure 6 for each grid cell (250 × 250 m) in the basin. Nitrate-N concentrations in water from wells sampled by the SRWMD do not necessarily correspond to areas of higher fertilizer application rates (Figure 6). However, median nitrate-N concentrations >1 mg/l in ground water from 10 of 11 wells are related to the amount of fertilizer applied upgradient from the well. An arbitrary upgradient area, representing a generalized contributing recharge area for each well, was delineated by orienting a semicircle (1000-m radius) perpendicular to the ground-water flow direction obtained from the potentiometric map of the UFA (Sepulveda *et al.*, 2006). The amount of N applied as fertilizers ranged from 4.9 to 13 kg/ha in these upgradient semicircular areas. Wells with nitrate-N concentrations >1.0 mg/l typically were located along the Ichetucknee Trace (Figure 2), an area of focused recharge and extensive limestone dissolution where the ancient Ichetucknee River once flowed before disappearing underground. Also, nitrate-N concentrations >3.0 mg/l were related to the percentage of closed depressions within the semicircular delineated areas. Three wells with nitrate-N concentrations >2 mg/l are located within 3 km of the discharge areas for six springs in the State Park. Although the spatial extent of the ground-water nitrate-N data is somewhat limited, there appears to be a relation between fertilizer application in closed depressions and nitrate concentrations in ground water within the basin.

The UFA in the springs basin appears to be most vulnerable to contamination in areas that contain closed topographic depressions (Figure 7). These depressions typically include sinkholes and other places where focused recharge to the aquifer occurs. Closed depressions encompass about 11% of the total area of the ISB. It is important to note that even though closed depressions encompass only 11% of the basin area, about 34% of the areas fertilized in the basin are in closed depressions that receive annually about 87,400 kg N.

Areas south of the Cody Scarp are particularly vulnerable to nitrate contamination from fertilizer applications on cropland because of the numerous closed depressions in the karst plain that concentrate recharge to the aquifer. Delineation of sensitive areas is an effective first step in protecting the UFA from further contamination (Canter, 1997). Vulnerability of the UFA in the springs basin to contamination from cropland fertilizer application was grouped into three main categories: low, medium, and high. Low vulnerability areas are where the N load is <34 kg/ha and contain no closed depressions. Medium vulnerability areas are where the N load is >34 kg/ha and contain no closed depressions, or areas where the N load is <34 kg/ha in areas with closed depressions. High vulnerabilty areas are where there are numerous closed depressions and the N load is >34 kg/ha. There are numerous areas of medium vulnerability

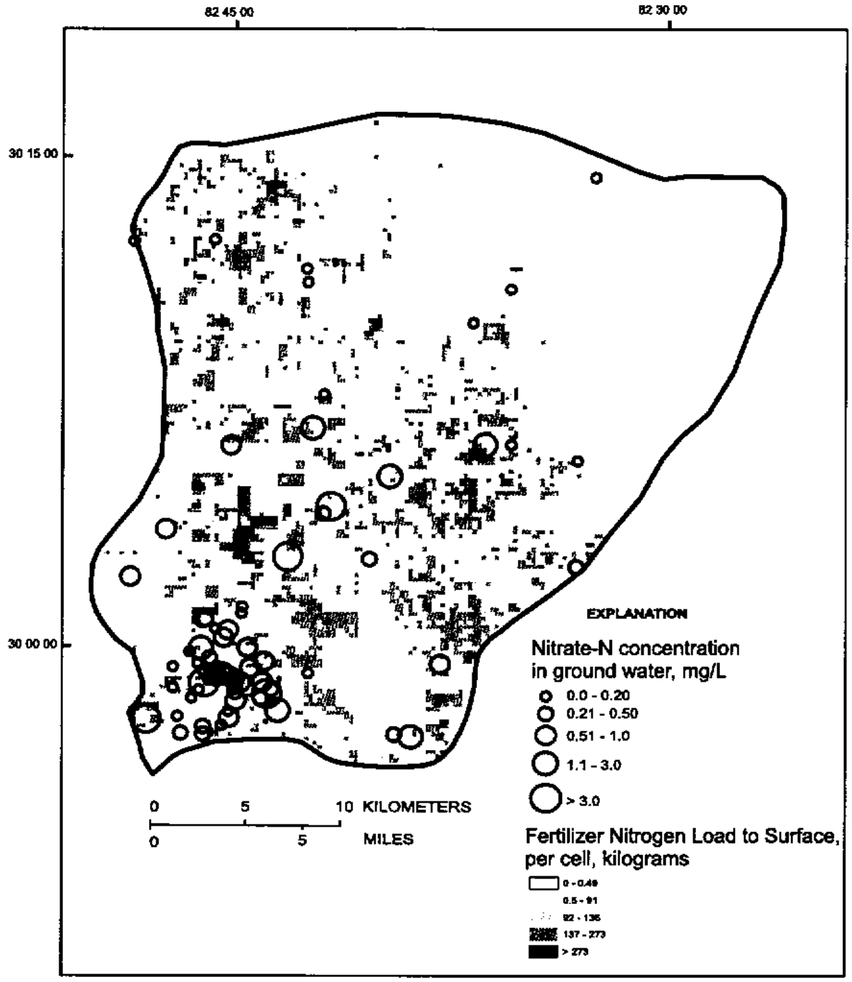

FIGURE 6. Map Showing Nitrogen Loads From Fertilizers, Animal Wastes, and Septic Tanks in the Ichetucknee Springs Basin.

within 4 km of the springs and an area of high vulnerability within 12 km from the springs (Figure 8). Reduction of N inputs from fertilizers in these areas would likely result in lower nitrate concentrations in ground water and spring waters over time.

CONCLUSIONS

In response to concerns about steadily increasing nitrate concentrations over the past several decades in northern Florida spring waters, a detailed N mass-balance budget was developed for the 960-km^2 karstic Ichetucknee Springs basin. This budget was based on measurements of N species in rainfall at two locations in the basin, ground water and spring waters, along with N loading estimates to ground water from fertilizers, septic tanks, dry deposition, animal wastes, and the land application of wastewater and wastewater solids. Fertilizers applied to cropland, yards, and pine stands contribute slightly more than 50% of the estimated total N load to ground water (592,000 kg/year) in the springs basin. Dominant loading from fertilizers is consistent with N-isotope data for spring waters (δ^{15}N-NO_3 = 3.3 to 6.3‰), elevated potassium concentrations in ground water, and are consistent with estimated historic N inputs for Columbia County. Other sources contribute the following percentages of the total estimated N load to ground water: animal wastes (29%), septic tanks (10%), atmospheric deposition (9%), and wastewater and biosolids applied to the land surface (2%). Due to below normal rainfall during the study period (97.3 cm), N loading values from atmospheric deposition were about 30% lower than that for normal rainfall amounts (136 cm). Approximately, 266,000 kg N/year was exported from the ISB by spring waters.

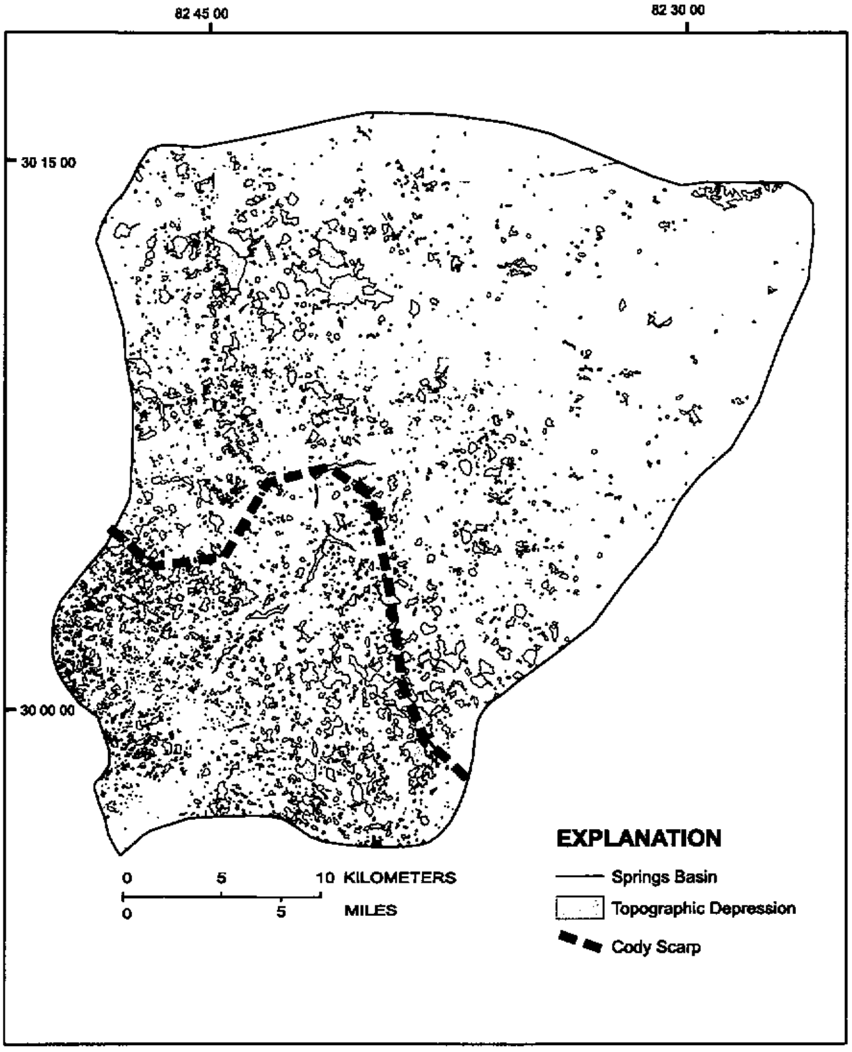

FIGURE 7. Map Showing Location of Closed Topographic Depressions in the Ichetucknee Springs Basin.

Admittedly, annual N loading estimates to ground water from the various sources in the basin are based on several arguable hypotheses, and on a range of N loss estimates from literature studies in varied hydrologic settings. However, when minimal N leaching estimates (10-20%) are assumed that are consistent with other studies, estimated annual N loading to ground water (260,000 kg) was similar to estimated N exported from the basin in spring waters (266,000 kg). Excess estimated annual N input loads to ground water may result from an overestimation of N inputs from fertilizers and other sources, and/or N storage in soils and the unsaturated zone beneath fertilized areas, and long ground-water residence times that do not reflect current land use.

Spatial loading from fertilizers, evaluated using a geographically based model grid (155 rows and 157 columns of 250 by 250-m cells), provided a quantitative vulnerability estimate for nitrate-N contamination of spring waters. Areas in the southern half of the basin, south of the Cody Scarp, are particularly vulnerable to nitrate contamination from fertilizer applications on cropland due to numerous closed depressions. High vulnerability areas to nitrate contamination have numerous closed depressions and N application rates are 34 kg/ha/year and higher. Numerous areas of medium vulnerability to contamination occur within 4 km of the springs, and an area of high vulnerability occurs within 12 km of the springs.

Reducing fertilizer inputs would substantially lower N loading to ground water over time. However, continued leaching of N to ground water from that potentially stored in the subsurface could mask any immediate decrease in ground-water nitrate concentrations from future reductions in fertilizer use to the

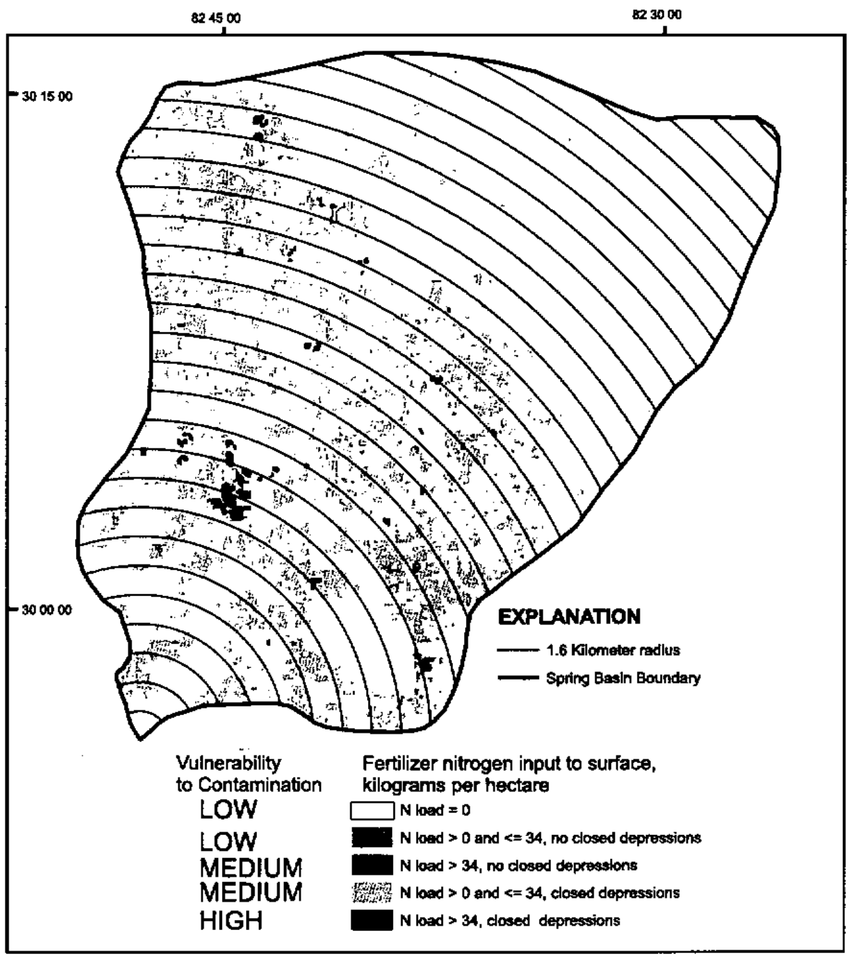

FIGURE 8. Map Showing Areas of Low, Medium, and High Vulnerability for Nitrate-N Contamination of Ground Water From Fertilizer Applications to Cropland.

basin, as studies have shown that ground water discharging to springs has residence times on the order of decades. The N budget presented in this study is a first step in quantifying loads from different sources and assessing vulnerable areas in the basin. Future studies need to address uncertainties associated with N leaching, particularly regarding transformation of N species in the subsurface from various input sources.

ACKNOWLEDGMENTS

This study was funded jointly by the Florida Department of Environmental Protection and the U.S. Geological Survey. The authors thank D. Blum, L. Lewis, T. Petrosky, E. Rau, and M. Stephens for assistance with field work; the USGS National Water Quality Laboratory for chemical analyses of rain-water samples; T. Coplen for nitrogen isotope analyses; and C. Bersok, R. Hicks, L. Morse, P. Lee, C. Green, and two anonymous reviewers for their comments that were helpful in revising this manuscript.

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