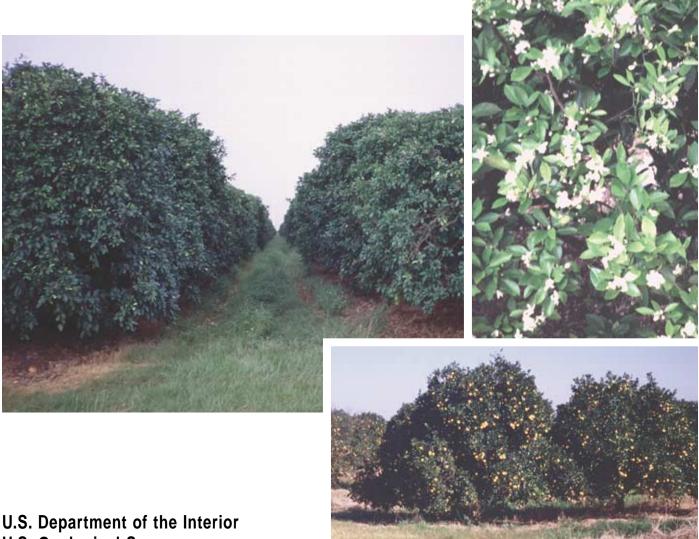


Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, **Florida**

Water-Resources Investigations Report 00-4057



U.S. Geological Survey

Prepared in cooperation with the Institute of Food and Agricultural Sciences, University of Florida

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By C.A. Crandall

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Prepared in cooperation with the INSTITUTE OF FOOD AND AGRICULTURAL SCIENCES, UNIVERSITY OF FLORIDA

Tallahassee, Florida 2000



U.S. DEPARTMENT OF THE INTERIOR BRUCE BABBITT, Secretary

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Multiply	Ву	To obtain
inch (in.)	25.4	millimeter
inch per year (in/yr)	25.4	millimeter per year
foot (ft)	0.3048	meter
foot per foot (ft/ft)	0.3048	meter per meter
acre	0.4047	hectare
pound per acre (lb/acre)	1.12	kilogram per hectare
million gallons per day (Mgal/d)	0.04381	cubic meter per second
		-

Conversion Factors, Acronyms, and Abbreviations

- DOC = dissolved organic carbon
- MCL = maximum contaminant level
 - SI = saturation indices
 - TU = tritium units
- USEPA = U.S. Environmental Protection Agency
- USGS = U.S. Geological Survey
- $\mu g/L =$ micrograms per liter
- mg/L = milligrams per liter
- $cm^3/L = cubic centimeter per liter$

Temperature can be converted between degrees Fahrenheit (F) and degrees Celsius (C) as follows:

 $^{\circ}F = 9/5 (^{\circ}C) + 32$ $^{\circ}C = 5/9 (^{\circ}F - 32)$

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, Florida

By C.A. Crandall

Abstract

The surficial aquifer system beneath citrus groves in Indian River, Martin, and St. Lucie Counties, Florida, was studied to determine the effects of citrus agriculture on ground-water quality. The surficial aquifer is the primary drinking-water source for Martin and St. Lucie Counties and furnishes about 33 percent of the drinking-water for Indian River County. Water-quality samples and water-level data were collected from December 1996 through October 1998. Nitrate concentrations in ground water exceeded 10 milligrams per liter (mg/L), the U.S. Environmental Protection Agency's maximum contaminant level for nitrate reported as nitrogen, in 5 percent of the samples from citrus groves. These exceedances occurred in samples from wells with depths of 10 feet or less at citrus groves, and mostly in samples collected during or immediately following fertilizer applications. Samples from wells with depths of 20-25 feet contained little or no nitrate. The decreased nitrate concentrations in ground water with depth was not consistent with chloride and dissolved-solids concentrations, two other common indicators of agricultural activity. Chloride and dissolved-solids concentrations remained elevated in ground-water samples from all depths at citrus groves; median chloride and dissolved-solids concentrations in samples from citrus sites were 125 and 779 mg/L. respectively. In comparison, samples from the reference site had maximum chloride and

dissolved-solids concentrations of 61 and 366 mg/L, respectively. Based on the age of ground water at 20-25 foot depths (3-50 years, measured with tritium and helium-3 concentration ratios). nitrate concentrations also should have remained elevated with depth because fertilizers have been used for at least 20-30 years at these citrus groves. Nitrate concentrations decreased with depth as a result of denitrification. This could have occurred because favorable conditions for denitrification existed in the aquifer, including high concentrations of dissolved organic carbon and iron (median concentrations of 25.5 and 1.75 mg/L, respectively at citrus sites) and low concentrations of dissolved oxygen (median concentration of 0.9 mg/L at citrus sites), which indicates that reducing conditions were present. Evidence that denitrification occurred included the enrichment of ground water with depth in the heavier isotope of nitrogen, nitrogen-15 (¹⁵N). Ground water from wells screened 10-15 feet below land surface had a median $\delta^{15}N$ value of 24.6 per mil, whereas ground water from wells screened 5-10 feet below land surface had a median δ ^{15}N value of 9.4 per mil. Fertilizer samples had a median δ^{15} N value of 3.0 per mil. Increased δ^{15} N values coincident with decreased nitrate concentrations with depth indicates that fractionation occurred during denitrification reactions. Finally, excess nitrogen gas, a byproduct of denitrification reactions, was detected at concentrations ranging from 0-8 mg/L in samples from wells screened 10-25 feet below land surface.

INTRODUCTION

Large quantities of nitrogen in fertilizers in various forms, such as ammonium nitrate $(NH_4 NO_3)$ and potassium nitrate (KNO_3) , are applied annually to citrus groves in Florida to improve the quality and production of fruit. Much of the nitrogen is readily converted to nitrate, a highly soluble and mobile species that has the potential to leach to underlying aquifers. The surficial aquifer is the primary drinking-water source in Indian River, Martin, and St. Lucie Counties (Alvarez and Bacon, 1988). Concern for public drinking-water supplies owing to the high application rates of nitrogen-containing fertilizers and the proximity of the water table to land surface in citrus-producing areas prompted this study.

Ground-water contamination from nitrogen in fertilizers has caused considerable concern in many agricultural areas in the United States and Europe (U.S. Department of Agriculture, 1991; McNeal and others, 1994, 1995; Mueller and others, 1995; Tucker and others, 1995; Graham and Alva, 1996). Several studies of water quality in citrus areas of central Florida have reported nitrate concentrations greater than the U.S. Environmental Protection Agency's (USEPA) maximum contaminant level (MCL) of 10 milligrams per liter (mg/L). Fifty to 100 percent of samples collected from shallow ground-water wells in citrus areas of Florida exceeded the USEPA MCL for nitrate (McNeal and others, 1994, 1995; German, 1996; Graham and Alva 1996). Nitrate concentrations in water from wells screened at deeper levels in the saturated zone were less than 10 mg/L (McNeal and others, 1995).

Factors that can affect nitrate distribution. movement, and fate in ground water include land-use patterns, agricultural practices, and soil characteristics. Changes in land-use patterns in Indian River, St. Lucie, and Martin Counties include substantial increases in citrus acreage. From 1966 to 1996, irrigated citrus acreage increased from 41.000 to 67.000 in Indian River County; from 22,000 to 47,000 in Martin County; and from 64,000 to 107,000 in St. Lucie County (Florida Agricultural Statistics Service, 1996, 1998). Agricultural practices also have changed. Agricultural practices vary by grove, based on fertilizer placement (over root zone or directly on trees), the timing of applications (in rainy season or not), the number of split applications per year, types of irrigation practices, and the form of nitrogen applied

(reduced ammonium or oxidized nitrate) (Tucker and others, 1995). Soil characteristics such as permeability, pH, and exchangeable bases, are variable from one grove to another and have a profound influence on the movement and fate of nutrients. In some areas with poorly drained soils, denitrification reactions (conversion of nitrate (NO₃) to N₂ or N₂O by microbial processes) are an important pathway for nitrogen loss from the subsurface, thus preventing excessive nitrate from reaching the deeper surficial aquifer.

In 1996, the U.S. Geological Survey began a cooperative study with the Institute of Food and Agricultural Sciences (IFAS), University of Florida, to evaluate the factors controlling nitrate concentrations in ground water in citrus-growing areas of Indian River, Martin, and St. Lucie Counties. The goals of this study were to determine the distribution, movement, and fate of nitrate in ground water at selected citrus groves.

Purpose and Scope

The purpose of this report is twofold: (1) to describe the distribution of nitrate and other constituents in ground water beneath citrus groves, and (2) to determine the fate of nitrate in the surficial aquifer system and its rate of lateral and vertical migration in ground water. Wells were installed in the surficial aquifer system and surface-water sites were established at six groves and one nonagricultural (reference) site. Water was sampled for nutrients, major ions, dissolved organic carbon, dissolved gases, and selected isotopes from the fall of 1996 through the summer of 1998. The groves were selected based on representative soil series; management practices; the age, health, and type of citrus trees; and the willingness of grove owners to cooperate with this study.

Acknowledgments

The author would like to thank Dr. Brian Boman, Marion Parsons, and the entire IFAS staff for their generous help and support, and the six citrus growers who consented to allow this study to occur on their property. The author also thanks the following U.S. Geological Survey employees: L. Niel Plummer and Carol Kendall for their insightful reviews, and Marian Berndt, Brian Katz, Gary Mahon, and J.K. Bohlke for their support and guidance on this project.

DESCRIPTION OF THE STUDY AREA

The study area is located within the Indian River citrus-production area in Indian River, Martin, and St. Lucie Counties, Fla., (fig. 1). The citrus production area in these three counties makes up nearly 286,000 contiguous acres of irrigated citrus crops. The area is adjacent to the Atlantic Coast in the central and southern part of the Flatwoods Physiographic Province (Caldwell and Johnson, 1982), which is characterized by poorly drained spodosol soils that have an organic horizon (Tucker and others, 1995). Soils in the Flatwoods Province are generally underlain by calcium carbonate deposits (Tucker and others, 1995).

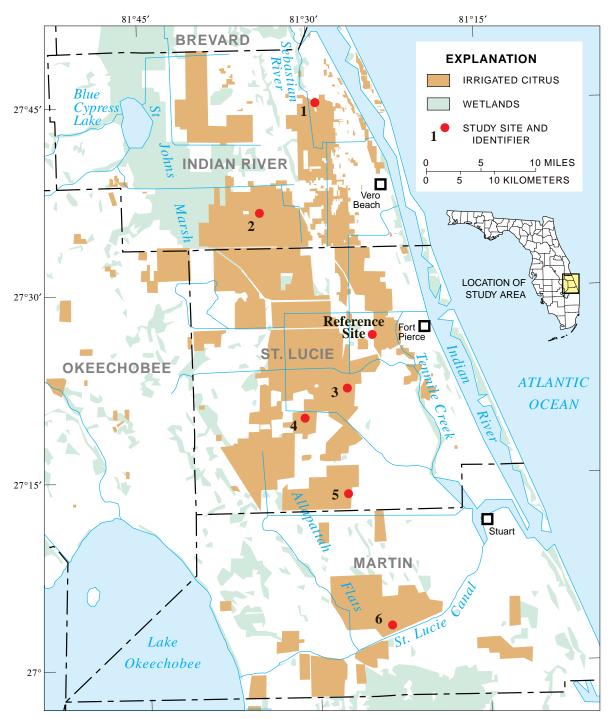


Figure 1. Citrus sites, reference site, and irrigated citrus areas, Indian River, Martin, and St. Lucie Counties, Fla.

The climate of the study area is characterized as subtropical humid with long, warm, and mostly wet summers and short, dry winters. Mean annual temperatures range from 72.4 °F at Vero Beach to 74.1 °F at Stuart, Fla., (Owenby and Ezell, 1992). Most years have few days of frost or freezing temperatures. Approximately 60 percent of all rainfall occurs between June and October (Schiner and others, 1988); summer rainfall is due to convective activity whereas winter rainfall is due to large continental cold fronts. Occasionally, tropical storms or hurricanes may produce up to 10-20 inches (in.) of total rainfall, substantially increasing the annual total (Schiner and others, 1988). Average annual rainfall is 50.06 in. at Fort Pierce, 53.08 in. at Vero Beach (station 4W) and 54.32 in. at Stuart, Fla., (Owenby and Ezell, 1992). In 1997, pan evaporation measured at Vero Beach was 63.28 in. (National Oceanic Atmospheric Administration, 1997). Pan evaporation commonly is greater than actual evapotranspiration (to get a more accurate estimate of actual evapotranspiration, pan evaporation is usually multiplied by 0.7). Evapotranspiration has been estimated to average 42 in. per year in Indian River County (Schiner and others, 1988).

Land-surface altitudes in Indian River, St. Lucie, and Martin Counties generally are less than 30 feet (ft) above mean sea level (Earle, 1975; Miller, 1978; Schiner and others, 1988); altitudes average about 28 ft above mean sea level. Land-surface altitudes range from 0-60 ft in St. Lucie County (Bearden, 1972), from 0-50 ft in Indian River County (Schiner and others, 1988), and from 0-20 ft in Martin County (Lichtler, 1957).

Hydrogeology

The top 700-1,500 ft of sediments composing the study area range in age from Eocene to Holocene and form the surficial and Floridan aquifer systems (table 1). The uppermost undifferentiated sediments consist of up to 100 ft of unconsolidated sand, clay, coquinas, and organic material (Miller, 1978; Schiner and others, 1988). Below the undifferentiated sediments are the Anastasia, Fort Thompson, and Caloosahatchee Formations of Pleistocene age and the Tamiami Formation of Pliocene age, which total 100-400 ft in thickness (Lichter, 1957; Miller, 1978; Miller, 1986; Schiner and others, 1988). The Anastasia, Fort Thompson, and Caloosahatchee Formations generally consist of sand, coquina, limestone, marl, and sandstone (Schiner and others, 1988). The Tamiami Formation consists of clay, sandy clay, and shells with some cemented zones. These post-Miocene-age strata form the surficial aquifer system, which is bounded beneath by the Hawthorn Group of Miocene age; the Hawthorn Group forms the intermediate confining unit of the Floridan aquifer system. Below the intermediate confining unit lies the Floridan aquifer system, which consists of the Suwannee and Ocala Limestones and the Avon Park and Oldsmar Formations. The Suwannee Limestone of Oligocene age underlies the Hawthorn Group in parts of the study area; in other areas, where the Suwannee Limestone is missing, the Ocala Limestone of Eocene age underlies the Hawthorn Group. The Avon Park and Oldsmar Formations of Eocene age underlie the Ocala Limestone and make up the lower part of the Floridan aquifer system (Schiner and others, 1988).

System	Series	Stratigraphic Unit	Hydrogeologic Unit	
	Holocene	Undifferentiated sediments		
Quatamany		Anastasia Formation		
Quaternary	Pleistocene	Fort Thompson Formation	Surficial aquifer system	
		Caloosahatchee Formation		
	Pliocene	Tamiami Formataion		
	Miocene	Hawthorn Group	Intermediate confining unit	
Tertiary	Oligocene	Suwannee Limestone		
Tertiary		Ocala Limestone	Floridan aquifer system	
	Eocene	Avon Park Formation		
		Oldsmar Formation		

Table 1. Generalized geologic sections and hydrogeologic units in east-central Florida

 [Lichtler, 1960; Miller, 1986; Schiner and others, 1988]

In the study area, the surficial aquifer system generally is unconfined; however, locally, it may be confined or semiconfined where beds of low permeability are present (Schiner and others, 1988). The water table usually is within 5 ft of the surface (Izuno and others, 1988). Most natural recharge to the surficial aguifer system is from rainfall. The surficial aguifer system can receive discharge from the Floridan aquifer system where the upper confining unit is leaky; water in the Upper Floridan aquifer is under artesian pressure in the study area. The surficial aquifer system responds rapidly to rainfall or to drought (Izuno and others, 1988). The natural potentiometric surface of the surficial aquifer system (equivalent to the water table) roughly approximates land surface topography (Healy, 1982). The water table usually lies within 1-2 ft of land surface in flat, poorly drained areas such as Indian River and St. Lucie Counties. The water table usually is deeper in Martin County (8-10 ft below land surface) (Healy, 1982). Natural discharge from the surficial aquifer system occurs as evapotranspiration, discharge to canals, and discharge to the Indian River, St. Johns Marsh, (Earle, 1975; Schiner and others, 1988), Tenmile Creek, Allapattah Flats, St. Lucie Canal, or Sebastion River (Miller, 1978; Kane, 1992a,b). Seepage of shallow ground water from the surficial aquifer system to the extensive network of local drainage canals has been estimated to range from 0.3-2.8 cubic feet per second per mile per foot of head difference between ground water and the canal (Beardon, 1972). Water levels in the surficial aquifer system fluctuate continuously as a result of changes in recharge and discharge. Water levels also may fluctuate in response to pumping and manipulation through the canals in the study area (Schiner and others, 1988).

The surficial aquifer system is the primary source of drinking water in the study area (Earle, 1975; Miller, 1978; Schiner and others, 1988; and Marella, 1999). Water from the Floridan aquifer system, which is commonly the source of drinking water in Florida, tends to be high in dissolved solids (sulfate, chloride, and sodium) in the study area, whereas water from the surficial aquifer system is low in dissolved solids (chloride and sodium) (Schiner and others, 1988; Marella, 1999).

Water Use and Supply

Total freshwater withdrawal in Indian River, Martin, and St. Lucie Counties was nearly 700 million gallons per day (Mgal/d) in 1995 (table 2; Marella,

1999). Of this total, 70 percent (485 Mgal/d) was withdrawn from surface-water sources and the remaining 30 percent (207 Mgal/d) was withdrawn from ground-water sources. Agricultural irrigation accounted for nearly 95 percent of the total surface water withdrawn (458 Mgal/d). Surface water in the study area largely consists of a network of canals augmented by ground water, rainfall, and water from Lake Okeechobee and the St. Johns River headwaters. In 1995, agricultural irrigation accounted for 63 percent of the ground water withdrawn (131 Mgal/d), most of which (80 percent; 105 Mgal/d) was obtained from the Floridan aquifer system. The source of most drinking water (public supply and domestic selfsupplied) in the three counties is ground water. The surficial aquifer system accounted for about 94 percent of the public-water supply for Martin and St. Lucie Counties in 1995. The surficial aquifer system and the Floridan aquifer system each accounted for about 33 percent of the public-water supply for Indian River County in 1995 (Marella, 1999).

Table 2. Water use in Indian River, Martin, and St. LucieCounties, Fla., 1995

[Drinking water includes public supply and domestic self-supplied. Other includes commercial-industrial, self-supplied, recreation, and power generation. Withdrawals are in million gallons per day. () = percentage of water from the Floridan aquifer system. From Marella, 1999]

County	Ground water	Surface water	Totals
Indian River			
Agricultural irrigation	56.3 (90)	135.2	191.5
Drinking water	18.1 (33)	0.0	18.1
Other	2.2 (50)	1.1	3.3
Totals	76.6	136.3	212.9
Martin			
Agricultural irrigation	23.1 (75)	100.2	123.3
Drinking water	21.6 (6)	0.0	21.6
Other	5.1 (0)	20.1	25.2
Totals	49.8	120.3	170.1
St. Lucie			
Agricultural irrigation	51.5 (75)	222.1	273.6
Drinking water	24.5 (6)	0.0	24.5
Other	4.8 (0)	7.0	11.8
Totals	80.8	229.1	309.9
Indian River, Martin, and St. Lucie			
Agricultural irrigation	131.0 (81)	457.5	588.5
Drinking water	64.2 (14)	0.0	64.2
Other	11.9 (4)	28.1	40.0
Totals	207.1 (76)	485.6	692.7

Land-Use and Agricultural Practices

About 35 percent of Florida's irrigated citrus acreage is in Indian River, Martin, and St. Lucie Counties (Florida Agricultural Statistics Service, 1996). Although the total citrus acreage in the state decreased from 1966 to 1998, the total citrus acreage in Indian River, Martin, and St. Lucie Counties increased 170 percent (fig. 2) (Florida Agricultural Statistical Service, 1966, 1998). Soil and water resources in citrus groves are highly managed. Citrus groves on moderate to poorly drained soils, such as those in the study area, are bedded with rectangular blocks of trees (Jackson and others, undated; Ferguson and Taylor, 1993) (fig. 3). A bed is an elevated, mounded row of soil approximately 5 ft high and flattened on top. One to two rows of trees are planted on each bed. A block of trees contains 15-40 beds (15-80 rows of trees), and is approximately 220-240 yards long and 100-200 yards wide.

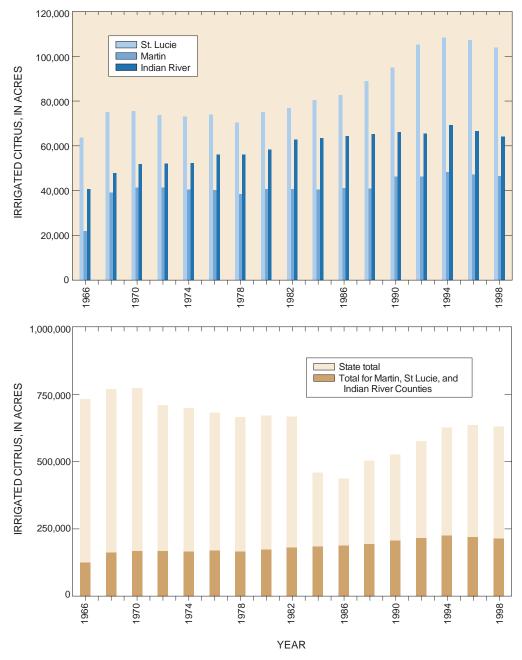


Figure 2. Irrigated citrus acreage in Indian River, Martin, and St. Lucie Counties, Fla., compared to each other and to total production, 1966-98.

6 Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, Florida

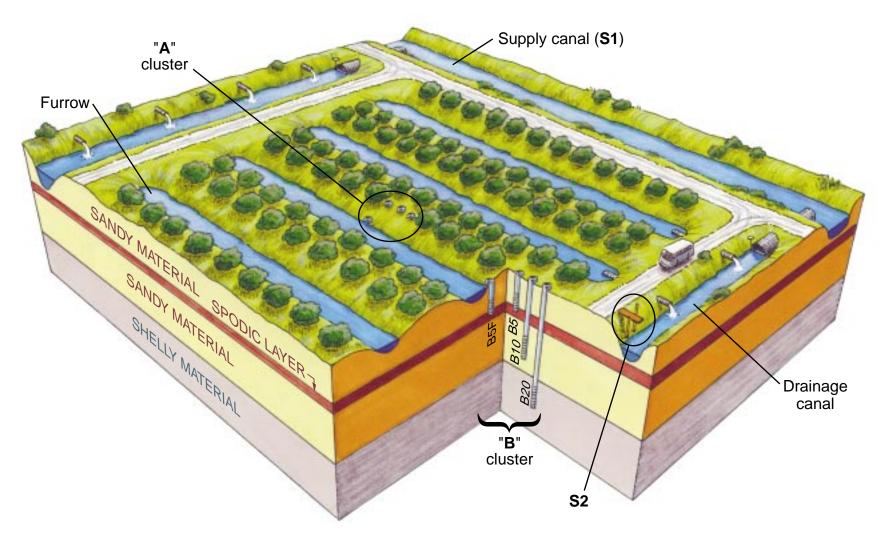


Figure 3. Typical citrus block showing beds, tree rows, canals, furrows, monitoring wells, and soil layers.



Figure 4. Drainage canal with furrow drain pipes extending out of the wall of the canal, St. Lucie County, Fla.

Trees typically are spaced 10-15 ft apart within rows and 24 ft apart between rows (Tucker and others, 1992; Ferguson and Taylor, 1993). Between each bed is a drainage ditch, or furrow, that conveys water to a nearby drainage canal (figs. 3 and 4). Irrigation water is delivered to the trees either through micro-irrigation or by seepage irrigation (fig. 5). Irrigation water usually is supplied by pumping water from a supply canal, which is commonly a separate canal on the site (fig. 3). Some supply canals also serve as drainage canals. Over half of all groves have irrigation systems designed to deliver fertilizers or pesticides through the irrigation systems (Ferguson and Taylor, 1993; Smajstrla and others, 1993). Irrigation systems are used more commonly during the spring because of the normally drier weather, coincident with the peak application period of fertilizers (Ferguson and Taylor, 1993). Citrus groves using seepageirrigation use furrows to provide both irrigation and drainage. Seepage irrigation entails filling furrows with water from the adjacent canal to near the top of the beds, thereby flooding the grove. This process usually takes 24 hours to complete. The high water level is maintained for approximately 1 day, and then the furrows are drained by pumping excess water to adjacent drainage canals (Smajstrla, 1993). The drainage process takes approximately 24 hours.



Figure 5. Microsprinkler irrigating a citrus tree, Martin County, Fla.

Approximately 175-225 pounds per acre (lb/acre) of nitrogen, generally as NH₄NO₃ or KNO₃ dry and liquid fertilizer formulations, is applied annually to groves. In most citrus operations, fertilizer is broadcast to the soil in two to three applications (McNeal and others, 1995). Most citrus growers use water-soluble dry fertilizer (Ferguson and Taylor, 1993); however, some growers use both liquid and dry fertilizer. Each year about one-third of the total annual nitrogen fertilizer is applied in the fall with the remaining two-thirds applied before June (Tucker and others, 1995). Other micro- and macro-nutrients, necessary for citrus health and nutrition, are applied with the nitrogen fertilizer. Other nutrients in fertilizer include carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, magnesium, sulfur, and calcium, boron, molybdenum, iron, manganese, copper, and zinc (Ferguson and Davies, 1995). Substantial amounts of chloride and sulfate are also included in fertilizers as salts. Calcium carbonate or dolomite also may be applied to soils to control soil pH-the target pH for optimal citrus health is 6.0 (Tucker and others, 1995).

METHODS

Sampling sites were established at six citrus groves in Indian River, Martin, and St. Lucie Counties; one reference site was established in St. Lucie County. Water samples were collected and analyzed for a variety of chemical and isotopic constituents to determine the water character. Water levels were measured monthly from December 1996 through July 1998 to determine flow patterns in the surficial aquifer. Hydrologic and chemical data were collected and statistical analyses were performed to determine water-quality trends and characteristics.

Site Selection

Sampling sites were selected based on representative soil properties, tree age and health, grove-management practices, distribution of groves throughout the study area, and the willingness of owner(s) to participate (table 3) (Boman and others, 1998; Boman, 1999). Sites were selected in areas representing the most common soil series used for citrus production in the three-county area-Riviera, Pineda, Wabasso, Oldsmar or related soil series. Blocks of trees were selected to minimize differences in tree size and age, as much as possible. Trees typically were 20-30 years old, and trees within each selected block were evaluated for health, uniformity, and type of fruit variety. Fruit produced within these six selected blocks included some of the most common orange and grapefruit varieties produced in the study area, such as Valencia oranges and Ruby-red grapefruit. Sites 1, 2, 4, 5, and 6 use micro-emitter sprinkler systems to deliver irrigation water, whereas site 3 uses seepage irrigation both microsprinkler emitter and seepage irrigation methods are common in the study area. Citrus blocks at sites 1, 2, and 4 are double-bedded (two tree rows per bed); blocks at sites 3, 5, and 6 are single bedded.

The selected sites included the most common soil series used to grow citrus in the study area. The soil series found at sampling sites 1, 2, 4, 5, 6, and the reference site include the Wabasso, Riviera, Pineda, Nettles, Oldsmar, and Pineda series, respectively, which are characterized as well-drained sandy to fine sandy soils. Soil series in the study area are differentiated by the presence of either a spodic or argyllic layer at depths of 30-40 in. below land surface, which can restrict or impede the downward movement of water (Watts and Stankey, 1980; McCollum and Cruz, 1981; Wettstein and others, 1987; Boman, and others, 1998).

Table 3. Primary soil series, management practices, and crop variety/vegetation for each sampling site, Indian River, Martin, and St. Lucie Counties, Fla. [FS, fine sand; LS, loamy sand; n/a, not applicable]

Site	Soil Series	Restricting layer	Planting date	Management practices	Row type	Crop variety/ vegetation
1	Oldsmar FS	Spodic	1964	Microspray	Double	Pineapple oranges
2	Riviera FS	Argillic	mid-1960's	Microspray	Double	Valencia oranges
3	Winder LS	Argillic	1920's	Flood irrigation	Single	Valencia oranges
4	Pineda sand	Argillic	mid-1960's	Microspray	Double	Ruby-red grapefruit
5	Nettles FS	Spodic	1965	Microspray	Single	White grapefruit
6	Wabasso FS	Spodic	mid-1960's?	Microspray	Single	Valencia oranges
Reference	Pineda sand	Argillic	n/a	n/a	n/a	Palmetto/pine

The Oldsmar (site 1), Nettles (site 5), and Wabasso (site 6) series are sandy soils containing spodic (organic) layers; whereas the Riviera (site 2) and Pineda (site 4) series are fine soils containing argyllic (clay) layers. Sampling site 3 is composed of the Winder series, a heavy, poorly drained loamy sand containing an argyllic layer (table 3) (Watts and Stankey, 1980; McCollum and Cruz, 1981; Wettstein and others, 1987). The reference site, located in a natural pine and palmetto savannah habitat, is underlain by Pineda soils. The reference site has never been used for any type of crop production (fig. 6).

Well Installation

During October and November 1996, wells were installed by using a portable hollow-stem auger and by following standard USGS procedures for the installation of water-quality monitoring wells (Lapham and others, 1995). At each of the six groves, two clusters of four wells each and, depending on supply and drainage canal arrangements, one or two surfacewater sites were established. At the reference site, six wells were installed in two clusters, and an adjacent surface-water site was established in a similar layout at the citrus sites.

At each site, an upgradient ("A") well cluster was located near the middle of the citrus block, usually 15-25 trees (100-200 ft) in from the end of the block (fig. 3). Surveying techniques were used to define relative northing, easting, and elevation coordinates at each site based on an arbitrary datum to compare water levels to compute hydraulic gradients between wells. The downgradient ("B") well cluster was located closer to the drainage canal, about two to three trees (20-50 ft) in from the end of the block. Within each cluster, wells were installed at the top of the beds between trees in tree rows at the following three depth intervals: (1) shallow, 4-10 ft deep (called A5 in the "A" cluster and B5 in the "B" cluster); (2) midlevel, 7-15 ft deep (called A10 in the "A" cluster and B10 in the "B" cluster); and (3) deep, 20-25 ft deep (called A20 in the "A" cluster and B20 in the "B" cluster).



Figure 6. Wells at the reference site in a natural pine and palmetto habitat, St. Lucie County, Fla.

An additional shallow well (called A5F in the "A" cluster and B5F in the "B" cluster) was located within or near the drainage furrow near each cluster at each citrus grove site; no furrow wells were installed at the reference site (fig. 3). The depths of the furrow wells ranged from 4-10 ft. Most were fitted with 2.5-ft-long slotted screens, but the midlevel wells at sites 1 and 4 were equipped with 5-ft-long slotted screens because of concern about poor well production (app. I).

Surface-water sampling sites were established along the supply canal (S1) and along the drainage canal (S2), which drains the studied bed (app. I). At site 2 and at the reference site, the same canal functioned as both irrigation supply and drainage canal for the studied blocks, so only one surface-water site was established.

Reference elevations, and northing and easting coordinates were established at each well and canal sampling point by using an arbitrary datum at each site. These elevations and coordinates were used to compare water-levels and compute distance and gradients. Reference coordinates and elevations are available in appendix I.

Water-Level Measurements

Water levels were measured monthly in most wells and twice monthly during peak fertilizer application periods. In furrow wells and drainage canals, water levels were measured quarterly and during sampling. Eight pressure transducers, one rain gage, and a barometric pressure logger were monitored at site 2 (except in well A5F) from May through October 1998 to determine relative surface-water elevations, waterlevel changes among wells and the drainage canal, and ground-water response to rainfall. Monthly total rainfalls was recorded at each site from 1996 through 1998.

Sample Collection and Analysis

Ground-water samples were collected by using a portable peristaltic low-volume pump outfitted with silicone-rubber tubing. Surface-water samples were collected using a steel drop sampler and polyethylene churn splitter. Rainfall samples were collected using a clean 5-gallon polyethylene bucket. Procedures outlined in Horowitz and others (1994) and Koterba and others (1995) were implemented in the collection of all samples and in the measurement of field parameters, including values of pH, temperature, specific conductance, and concentrations of dissolved oxygen (DO). Field parameters were measured onsite using portable meters with probes encased in a closed, flow-through chamber to prevent contact with the atmosphere.

In December 1996, water samples were collected from 43 wells, 11 canals, and a rainfall site near the reference site. Water samples could not be collected from 10 shallow and furrow wells and from the drainage canal at site 6 because the wells could not sustain pumping at this time and the canal was dry. Analyses included field parameters, major ions, nutrients, dissolved organic carbon (DOC), trace elements, and stable isotopes of oxygen and hydrogen. The rainfall sample collected during a storm event on December 8, 1996, was analyzed only for stable isotopes of oxygen and hydrogen.

In July 1997, a subset of wells and canals was sampled to determine if a seasonal component might exist in nitrate concentrations. Water samples were collected from the "A" cluster wells at sites 2, 5, and the reference site and from the drainage canals at these three sites. Water from 14 wells and three canals were analyzed for nutrients, field parameters, and stable isotopes of nitrogen in NO₃ and NH₄.

In May 1998, water samples were collected from 28 wells and 6 canals at sites 2, 4, 5, and the reference site. Additionally, three samples of dry fertilizer (one from each of the three citrus sites), a precipitation sample, and a microsprinkler-emitter sample (from site 5) were analyzed only for nutrients and/or stable isotopes of nitrogen, oxygen, and hydrogen. A rainfall sample was collected near the reference site following an overnight storm on June 8, 1998. Ground-water samples from shallow and furrow wells were analyzed for field parameters, major ions, nutrients, DOC, isotopes of oxygen, hydrogen, nitrogen, and carbon. Analyses in ground-water samples from midlevel and deep wells included major ions; nutrients; DOC; field parameters; dissolved gases; isotopes of oxygen, hydrogen, nitrogen, and carbon. Tritium and helium were analyzed in deep wells only. The number of sites had to be limited because of the cost associated with the extensive analyses performed on these samples. Sites 2, 4, and 5 were chosen for further study because of their representative soil and agricultural practices.

Analyses of major ions included calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), manganese (Mn), chloride (Cl), sulfate (SO_4) , bicarbonate (HCO₂), bromide (Br), fluoride (F), silica as (Si) SiO₂, and dissolved solids (DS). Nutrient analyses included concentrations of nitrite (NO₂), nitrate (NO_3) , ammonia (NH_4) , organic nitrogen (organic N), total phosphorus (total P), and orthophosphate (PO_4). In this report, concentrations of nitrogen and phosphorus species are reported in units of mg/L as nitrogen or phosphorus, respectively. Additionally, all nitrate values were computed as the sum of nitrate plus nitrite unless otherwise stated. Analyses of trace elements included arsenic (As), aluminum (Al), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), and zinc (Zn). Analyses of major ions, nutrients, dissolved organic carbon (DOC), and trace elements were conducted at the USGS laboratory in Ocala, Fla. Concentrations of major ions, nutrients, trace elements, and DOC are reported as dissolved species (operationally defined as able to pass through a 0.45µm filter). Ten percent of all samples collected were quality-assurance samples consisting of both field and equipment blanks and duplicate samples. Most of the sampling schedule is included in appendix II.

Analyses of dissolved gases included argon (Ar), oxygen (O_2), carbon dioxide (CO_2), nitrogen (N_2), methane (CH_4) and hydrogen sulfide (H_2S). Dissolved gas analyses were performed by the U.S. Geological Survey Dissolved Gas Laboratory in Reston, Va. Dissolved gas samples were collected by using methods developed by Pearson and others (1978) and Busenberg and Plummer (1992); H_2S samples were collected and analyzed in the field using a colorimetric method (methylene blue) and a portable field spectrophotometer (Hach Company, 1992). Dissolved gas analysis can be useful in determining the oxidation state of water and the likely occurrence of biogeochemical reactions (Korom, 1992).

Concentration ratios of stable isotopes of oxygen (¹⁸O/¹⁶O), hydrogen (²H/¹H) or the deuteriumprotium (D/P) ratio, carbon (¹³C/¹²C), and nitrogen (¹⁵N/¹⁴N) were determined in ground- and surfacewater samples. In this report, values of ¹⁵N/¹⁴N in NO₃ and NH₄ are reported as dissolved concentrations. Isotopic values were reported using standard δ (delta) notation (Gonfiantini, 1981) as defined by the following expression:

$$\delta$$
 (per mil) = [(R_{sample}/R_{standard}) - 1] * 1,000, (1)

for δ^{18} O, R = ¹⁸O/¹⁶O; for δ D, R=D/H; for δ^{13} C, R = ¹³C/¹²C; and for δ^{15} N, R = ¹⁵N/¹⁴N. Analyses of δ^{18} O, δ D, δ^{13} C, and δ^{15} N in water samples were performed in the USGS Isotope Fractionation Laboratory in Reston, Va.

Analyses of δ^{18} O and δ D were used in this study to determine mixing ratios along probable flow paths, based on water-level data, and sources of water. Measurements of δ^{13} C provide additional information on sources of carbon and potential rock-water interaction. For example, degradation of organic matter results in δ^{13} C values that are much lower than when the source of carbon is the dissolution of limestone (Katz and others, 1999). The carbon isotopic composition of most carbonate minerals is approximately 0 ± 5 per mil (Veizer and Hoefs, 1976); however, the carbon isotopic compositions of CO₂ in soils with similar natural vegetation and climate to the study area are generally -23.2 to -19.0 per mil (Rightmire and Hanshaw, 1973).

Nitrogen isotopic analyses are used primarily to determine sources of nitrogen in ground water. For instance, $\delta^{15}N$ of NO₃ values ranging from -2 to +3 per mil generally indicate inorganic fertilizer as the source of NO₃; $\delta^{15}N$ values ranging from +9 to +22 per mil indicate animal wastes as the source of nitrate (Kreitler and others, 1978). Enriched values of $\delta^{15}N$ may also be due to microbial reactions involving NO₃, such as denitrification. Ground-water NO₃ becomes enriched in the heavier isotope of ¹⁵N due to fractionation, a process by which microbes preferentially uptake NO₃ containing the lighter isotope, ¹⁴N (Mariotti and others, 1988).

The age of ground-water recharge (in years) was estimated by measuring tritium (³H) and tritogenic helium (³He or helium-3) concentrations in water and comparing these values to the long-term ³H-input function of rainfall measured at the International Atomic Energy Agency precipitation monitoring station at Ocala, Fla., (Michel, 1989). Tritium, with a half-life of 12.43 years, decays to ³He; by measuring ³H/³He, the ³H input can be corrected, improving the accuracy of the age of recharge estimate. Concentrations of ³H and ³He were determined only for samples from deep wells (20-25 ft) at sites 2, 4, 5, and the reference site because of the low yields from the shallower wells and the cost of the analysis. Water samples were collected and analyzed by using procedures developed by Michel (1989) and by Schlosser and others (1989). Equilibrium values of neon and non-tritogenic helium were used, when available and reasonable, to correct the age of water generated only from the ³H/³He ratios. Tritium, helium, and neon concentrations in water were determined by the Noble Gas Laboratory of the Lamont-Doherty Earth Observatory of Columbia University. Tritium activity is reported in tritium units (TU).

Data were described using nonparametric statistics, including the Kruskal-Wallis, Spearman correlation, and Tukey tests. P-values were calculated; values less than 0.05 were considered significant. Medians, maxima, mimima, ranges, boxplots, and x-y plots were utilized to describe data relations.

The chemical speciation program, PHREEQC (Parkhurst, 1995), was used to calculate calcite saturation indices. Input data included solute concentrations of major ions, nutrients, pH, dissolved oxygen, and temperature.

RAINFALL AND GROUND-WATER-FLOW PATTERNS

Ground-water-flow patterns must be determined in order to properly interpret geochemical data. Without velocity and directional information about water movement, geochemical interpretations may be in error. In the following discussion, rainfall patterns during the study are discussed and water levels are used to determine potentiometric gradients and direction of flow. Additionally, stable isotope data are used to estimate water sources, mixing ratios, and ages of recharge water.

Rainfall Patterns

Measured rainfall totals for 1997 and 1998 at the study sites generally were greater than but within 15 percent of annual long-term (1960-90) normal precipitation totals for Fort Pierce (50.06), Vero Beach (53.08), and Stuart (54.32), Fla., with the exception of site 1 (table 4; Owenby and Ezell, 1992). Annual longterm total rainfall data at the study sites were unavailable, so long-term NOAA climate station data from Stuart, Ft. Pierce, and Vero Beach were compared with rainfall at the study sites. Total rainfall for 1997 and 1998 at site 1 was 40 percent greater than the annual long-term normal for Vero Beach (table 4). Rainfall totals were lowest for the reference site. Rainfall during the study period generally was characterized by episodic flooding and drought conditions as a result of the El Niño and La Niña weather patterns. For example, although above average rainfall occurred in early 1998, severe drought conditions existed from March through May 1998, causing water levels in canals to drop, prompting the need for irrigation.

Ground-Water-Flow Patterns and Age of Water

Ground-water levels at site 2, which were measured from July through October 1998 using pressure transducers, were extremely variable and responded rapidly to rainfall and irrigation events (fig. 7). Water levels in the shallow wells (A5 and B5) responded slightly sooner and maintained higher water levels than midlevel or deep wells. Although significant correlation (p-value less than 0.01) was found between water levels in most of the wells, water levels in the B5F furrow well were more strongly correlated to the stage of water in the drainage canal.

At all citrus sites, hydraulic gradients indicated that water from shallow wells located on top of the beds moved rapidly downward toward midlevel wells and laterally and downward toward furrow wells. Water levels usually were highest in A5 wells at all sites except site 6, where water levels in the B5 well usually were higher than in other wells (fig. 8).

Table 4. Annual total rainfall for 1997 and 1998 and average annual rainfall, in inches,
at the citrus sites and at the reference site, Indian River, Martin, and St. Lucie
Counties, Fla.

Year	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Reference site
1997	80.3	61.0	60.9	63.9	55.8	61.9	49.6
1998	68.4	61.6	55.3	56.7	59.2	62.9	53.3
Average	74.4	61.3	58.1	60.3	57.5	62.4	51.5

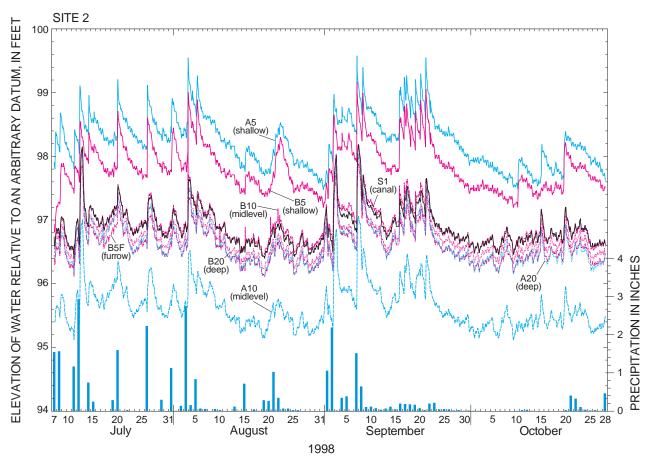


Figure 7. Hourly water levels in wells and canal at site 2, July through October 1998, Indian River County, Fla.

Vertical gradients from A5 and B5 wells to furrow wells (A5F and B5F, respectively) ranged from 0.002-9.8 foot per foot (ft/ft); units of vertical and horizontal gradient were calculated by dividing the vertical difference in water elevation by the difference in the depth or the distance between wells, respectively. Median gradients were then calculated for each pair of wells. Vertical gradients were greatest between shallow and furrow wells; gradients were 0.9 and 4.9 ft/ft at sites 2 and 6, respectively. Vertical gradients may have been greatest at these two sites due to the thicker spodic or argyllic soil layers. Tucker and others (1995) found that water tended to move rapidly downward during rainfall or irrigation until encountering a spodic or argyllic horizon, where it began moving laterally.

Exceptions to predominant flow patterns were also detected. Water levels in the A5F well generally were higher than water levels in the A5 wells at site 4, and water levels in the A20 wells at sites 2, 3, and 5 were higher than water levels in the A5 wells in about 50 percent of the measurements. These water levels indicate that, for a substantial period of time, the potential existed for water to move upward from deeper wells toward shallow (A5) wells at these sites (fig. 8). Downward gradients usually were present between shallow, midlevel, and deep wells. Median vertical gradients from the shallow to midlevel wells ranged from 0.09-0.45 ft/ft.

At the citrus sites, vertical water flow was much slower and the patterns more variable in the midlevel and deeper parts of the aquifer. Downward water movement from the midlevel wells to the deep wells was not common but did occur—for instance at site 2, water levels in the B10 well were higher than those in the B20 well 100 percent of the time (the median difference between water levels in wells B10 and B20 was 0.13 ft). Water levels in midlevel wells were higher than water levels in deep wells in 50 percent or more of the measurements at sites 1, 2, and the reference site (fig. 8). Vertical gradients between midlevel and deep wells ranged from 0.01-0.08 ft/ft. At the four remaining sites, water levels in midlevel wells were equal to or less than water levels in deep wells and, as a result, the composition of water from midlevel wells was more likely to be a mixture of water from shallow and deep wells.

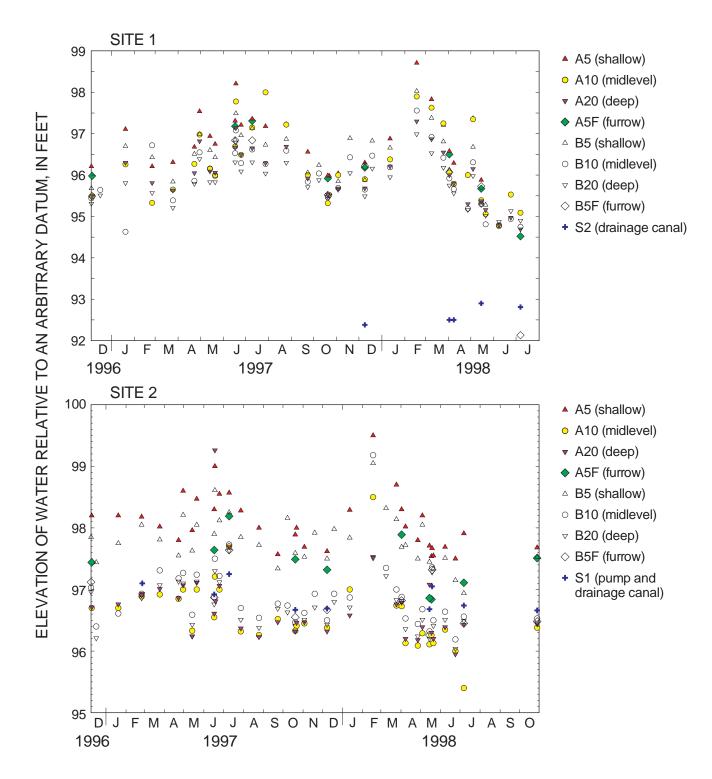


Figure 8. Water levels measured at the reference and citrus sites, December 1996 through July 1998, Indian River, Martin, and St. Lucie Counties, Fla.

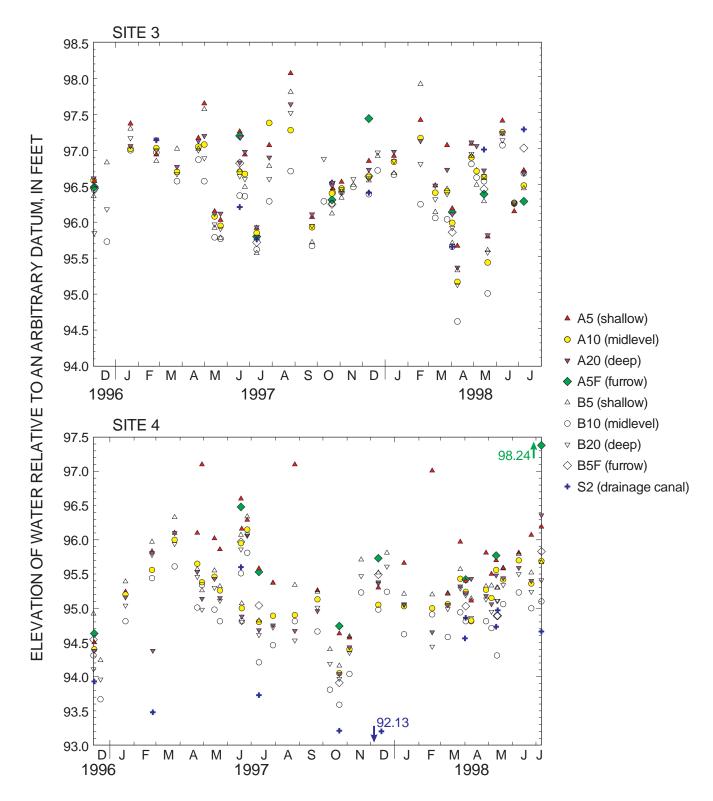


Figure 8. Water levels measured at the reference and citrus sites, December 1996 through July 1998, Indian River, Martin, and St. Lucie Counties, Fla. (Continued)

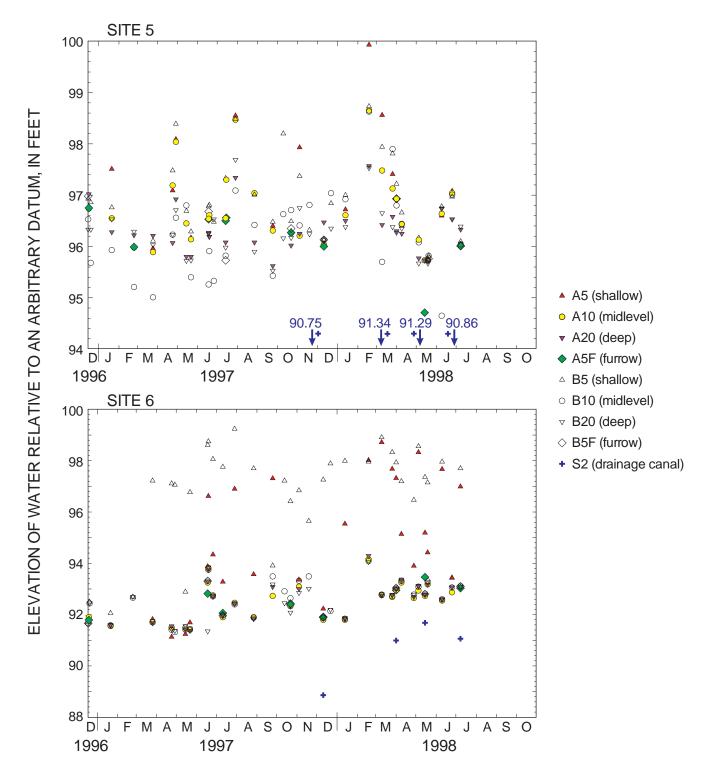


Figure 8. Water levels measured at the reference and citrus sites, December 1996 through July 1998, Indian River, Martin, and St. Lucie Counties, Fla. (Continued)

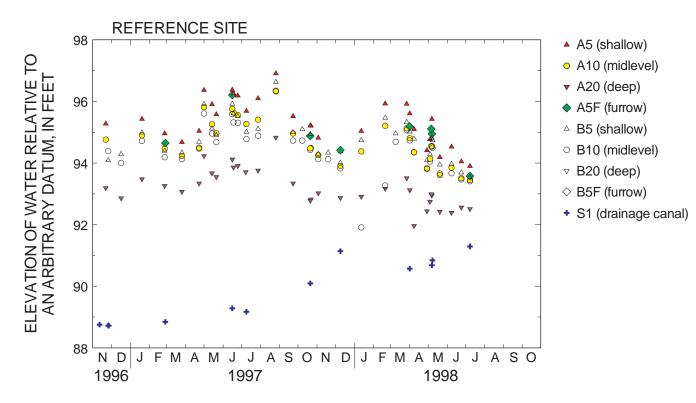


Figure 8. Water levels measured at the reference and citrus sites, December 1996 through July 1998, Indian River, Martin, and St. Lucie Counties, Fla. (Continued)

Horizontal gradients were generally one to two orders of magnitude lower than vertical gradients. However, between the "B" cluster wells and drainage canals, horizontal gradients were comparable in magnitude to the lower vertical gradients, ranging from 0-0.09 ft/ft. Water levels in A5 wells usually were higher than those of B5 wells, indicating that water at shallow well depths generally moved from the "A" to the "B" cluster, except at sites 5 and 6 where gradients were reversed (0.001 and 0.02 ft/ft, respectively).

Other generalizations about horizontal groundwater circulation patterns at the midlevel and deepwell depths were difficult to make because no predominant flow direction prevailed. In furrow wells, water generally moved from the B5F to the A5F wells. In the deeper wells, water typically moved from the A20 to the B20 wells at sites 1, 3, and 4, although horizontal gradients were low, ranging from 0.005-0.007 ft/ft. Generally, water moved from the B20 to the A20 wells at sites 2 and 6 where horizontal gradients ranged from 0.002-0.003 ft/ft. At site 5, ground-water gradients between the A20 and B20 wells were reversed at least 50 percent of the time probably due to raised canal water levels. At all but one of the sites, water levels in deep wells were higher than water levels in the drainage canal (fig. 8). At site 2, water levels in wells A20 and B20 were lower than or equal to water levels in the drainage canal (S1).

Isotopes

Isotopes of carbon, oxygen, hydrogen, and helium are useful in determining (1) the source of water, (2) mixing ratios, and (3) the age of water. Carbon in ground water resulting from the dissolution of carbonate minerals, is enriched in the heavier isotope of carbon, carbon-13 (^{13}C) , whereas carbon in ground water resulting from the decay of organic matter, is depleted in the heavier isotope. Carbon sources may be identified using this information. Stable isotope ratios of oxygen and hydrogen can be used to estimate mixing ratios if valid flow paths are identified from water-level data, and if sources of water have independent signatures. Tritium and helium-3 can be used to estimate the age of recharge water, which is important in identifying land-use practices that may affect water quality at the time of recharge.

Carbon, Oxygen, and Deuterium

Ratios of ${}^{13}C/{}^{12}C$ were analyzed and calcite saturation indices were calculated for samples collected in May 1998 from sites 2, 4, 5, and the reference site to determine the source of water. Carbon in ground water is derived mainly from carbonate minerals in sediments, soil humus, and the decay of landplant biomass (Coplen, 1993). The δ^{13} C values of most carbonate minerals is usually 0 ± 5 per mil (Veizer and Hoefs, 1976), whereas in areas with natural vegetation and climate similar to that of the study area, the δ^{13} C values of soil CO₂ range from -23.2 to -19.0 per mil (Rightmire and Hanshaw, 1973). Calcite saturation indices were calculated using PHREEQC (Parkhurst, 1995), a geochemical speciation and mixing model. Calcite saturation indices are likely to be near zero when ground water is at equilibrium with the mineral calcite in the aquifer. Negative indices indicate that water is undersaturated and is theoretically capable of dissolution of calcite, whereas positive indices indicate that water is oversaturated with respect to calcite and is theoretically capable of precipitation.

The $\delta^{13}C$ values plotted against calcite saturation indices (SI) show two distinct zones of water—one zone that is undersaturated with calcite and depleted in $\delta^{13}C$ and a second zone that is near saturation with

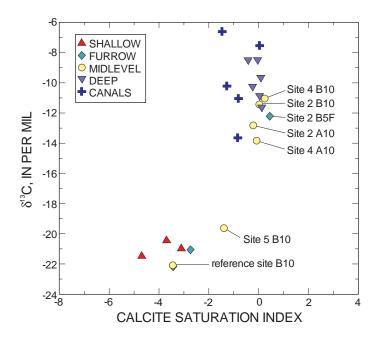


Figure 9. Values of delta ¹³C and calcite saturation index, by site and well, May 1998.

calcite and enriched in δ ^{13}C (fig. 9). Water from the shallow wells and a few midlevel wells generally was depleted in δ^{13} C (between -19 and -23 per mil) and undersaturated with calcite (SI values less than -2); which indicated that organic carbon, converted to CO_2 in various microbial reactions, was the most likely source of carbon. Water from deep wells (A20 and B20) and water from the canals generally was saturated with respect to calcite (SI values between -1 and 1) and was more highly enriched in δ^{13} C (values between -6 and -14 per mil; fig. 9). Water from deep wells and water from the canals may be a mixture of water from the shallow depleted zone and from a deeper part of the aquifer where the carbonate mineral content is high. Water from the midlevel wells and from one furrow well seems to be a mixture of water from deep wells (or canals) and water from shallow wells. The similarity of δ^{13} C and calcite saturation indices between water from canals and water from the deep wells indicates that one of these is either the source of water for the other or they share a common source of water. Water-level measurements at most citrus sites indicate that water occasionally moves laterally from the deep wells to the drainage canals and vertically upward to the midlevel wells.

> Results of δ^{18} O and δ D analyses also suggest that mixing may occur in midlevel and some deep wells at sites 2 and 5. At other sites, δ^{18} O and δ D values indicate that mixing has occurred, however, plausible mixing scenarios could not be developed because of disagreement with water-level and gradient data. Mixing ratios of water were calculated for plausible flow paths using δ^{18} O and δ D values from samples collected in May 1998. Results for site 2 indicate that water from well A10 may have been composed of about 40 percent water from A5 and 60 percent water from A20 (using δ D to compute mixing ratios; fig. 10). At site 5, water from A5 and B20 may have contributed 46 and 54 percent, respectively, of the water to well A20. Canal water may have been another contributing water source or may have been composed of deep well water that had undergone evaporation.

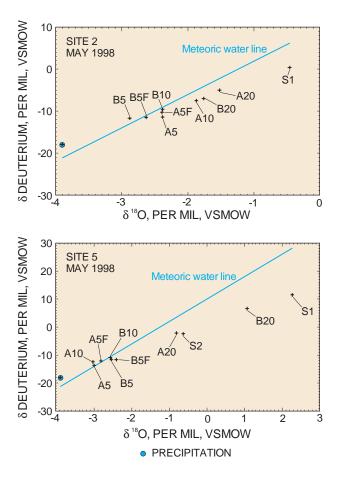


Figure 10. Values of delta ¹⁸O and delta deuterium at sites 2 and 5, May 1998.

Tritium and Helium-3

Concentrations of ³H and ³He were analyzed in samples from deep wells (19-24 ft deep) to estimate age of recharge water and velocity of water in the aquifer. Values of ³H and ³He can be useful for age dating. In the early 1950's, ³H was introduced in large quantities to the atmosphere when atmospheric testing of nuclear weapons began; before the 1950's, concentrations in ground water did not exceed 0.2 TU. Since reaching a peak during 1963-64, ³H concentrations in the atmosphere and in precipitation have declined with few exceptions in response to the cessation of aboveground nuclear testing in the 1970's (Michel, 1989). Atmospheric ³H was introduced to ground water through recharge. Because the radioactive decay of ${}^{3}\text{H}$ produces tritogenic helium (³He), measurements of the ${}^{3}\text{H}/{}^{3}\text{He}$ ratio in ground water provides a more reliable estimate of the age of young water (less than 30 years old) than the measurement of ³H alone (Plummer and

others, 1998). Fractionation from biological activity is generally not a concern in ³H and ³He concentrations (Plummer and others, 1992).

Measurements of neon and non-tritogenic helium concentrations (used to correct ${}^{3}H/{}^{3}He$ ages) were not possible in some samples and may have been due to gas stripping. This occurs when the total pressure of gases in ground water exceeds 1 atmosphere and the suction pressure of the pump is not high enough to keep the gases in solution; helium and other gases can bubble out of solution and adhere to the sidewalls of the sampling tube.

Ground water was generally oldest at sites 5 and 2 and youngest at site 4 and the reference site indicating that water may travel more slowly, have a longer flow path, and(or) a greater component of water may originate from deeper in the aquifer at sites 2 and 5 compared to site 4 and the reference site (table 5). Vertical ground-water velocities were estimated from water ages and well depths. The average vertical velocity of water at sites 2 and 5 was similar (ranging from 0.4-1.0 ft/yr, respectively) and much slower than the average vertical velocities at site 4 and the reference site (ranging from 2.0-8.5 ft/yr, respectively). Similarities in the soil profiles would explain the similar vertical velocities at sites 2 and 5: site 5 is underlain by a 20-in-thick spodic layer, the top of which is approximately 3 ft below land surface; site 2 is underlain by a 30-in-thick argyllic layer that is about 2 ft below land surface. Both site 4 and the reference site are located on Pineda soils, which contain 12-15 in-thick argyllic layers lying within about 1 ft of land surface. Breaches from decayed root channels or other causes are common in this layer and can facilitate rapid infiltration and transport of water.

Table 5. Tritium age, corrected age of recharge water, andvertical velocity of ground water in deep wells at selected sites,May 1998

[ft/yr, foot per year; --, unable to measure]

Site Well		Date	Tritium/ Helium-3 age (years)	Corrected age (years)**	Vertical velocity (ft/yr)
2	A20	5/18/98	14.8 ±0.6	19.7 ±0.8	1.0
	B20	5/19/98	15.6 ±0.9	22.8 ±1.2	0.9
4	A20	5/11/98	7.2 ±0.5	10.2 ±1.0	2.3
	B20	5/12/98	2.6 ±0.4		8.5*
5	A20	5/20/98	31.8 ±7.4	24.4 ±7.3	0.8
	B20	5/14/98	51.8 ±0.6	48.9 ±2.6	0.4
Reference	A20	5/6/98	5.1 ±0.8		4.1

* Uncorrected tritium age used to compute vertical velocity.

** Age of water corrected using equilibrium values of neon and non-tritogenic helium.

DISTRIBUTION OF NITRATE AND OTHER AGRICULTURAL CONSTITUENTS

Factors that can affect the chemical composition of ground water include quality and quantity of rainfall as recharge, aquifer properties such as rock type and permeability, circulation patterns in the aquifer, leakage or recharge from deeper aquifers, and land-use practices. Chemical composition and water quality were evaluated by analyzing major ions, trace elements, and nutrients (nitrogen and phosphorus). Oxidation conditions were evaluated based on dissolved-gas data.

Major Ions

Distinct differences were noted between the major ion composition of ground water and surface water at the six citrus sites compared to that of the reference site. Eighty-one percent of all samples consisted of a mixed water type (no dominant ions), and water types were consistent between groves during low and high fertilization periods (table 6; fig. 11). Water is designated as a "mixed" water type when no single cation or anion makes up more than 60 percent of the sum of equivalent cations and anions. A cation or anion is considered a dominant ion when the percentage of the ion is greater than 60 percent of the total cation or anion concentration. The predominance of mixed water types for samples from the citrus sites contrasts sharply with the water types for samples collected from the reference site; only 1 of the 12 samples collected at the reference site (8 percent) was a mixed water type (table 6).

Table 6. Geochemical water types, December 1996 and	ł
May 1998	

Туре	Distribution (number of samples)						
of well	Mixed*	Ca, Mg, SO ₄	Ca, HCO ₃	NaCl	Mixed Cl	Mixed HCO ₃	
Citrus							
Shallow	9	1			2		
Furrow	9					1	
Midlevel	15		1		2		
Deep	16		2				
Floridan				1			
Surface water	11				4		
Reference							
Shallow	1			2	1		
Midlevel				1	3		
Deep			2				
Surface water			1			1	

*Mixed water type indicates that no single cation or anion makes up more than 60 percent of the total cation or anion composition, in milliequivalent per liter.

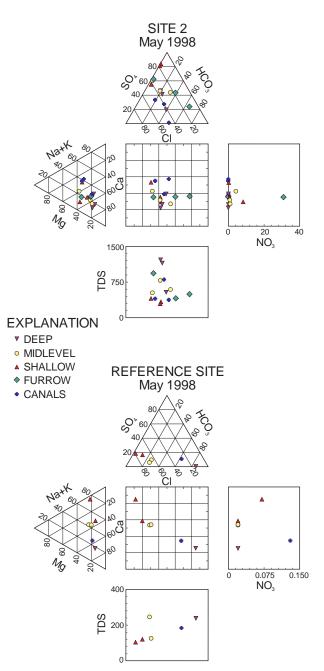


Figure 11. Major ion distribution, nitrate, and dissolvedsolids concentrations on Durov diagram for site 2 and the reference site, May 1998.

The predominance of mixed water types associated with citrus areas may reflect the contribution of irrigation water and the addition of fertilizers to the soil—masking the natural water types. Samples from shallow wells at the reference site consisted either of a Na-Cl or a mixed-Cl water type, suggesting that rainfall was the dominant source of water. Ground water from the deep well at the reference site and from two deep wells at the citrus sites was a Ca-HCO₃ type, suggesting the presence and dissolution of carbonate aquifer materials approximately 20 ft below land surface.

Concentrations of most major ions in ground water and surface water (canals) were significantly higher at the citrus sites compared to the reference site (table 7; fig. 12). Potassium concentrations were highest in samples from midlevel and shallow wells at the citrus sites; median concentrations at these two well depths were 14 mg/L each (table 8). Potassium concentrations were lowest in samples from the reference site (median of 0.8 mg/L; table 7). Calcium and bicarbonate concentrations were significantly higher in the deep wells at all sites probably reflecting the fact that these wells were screened in shelly (limestone) materials. Only concentrations of DO, iron, ammonium, and total phosphorus measured in samples from the reference site were both similar in magnitude and distribution to concentrations in samples collected from the six citrus sites. Water-quality data are presented in appendix III.

 Table 7.
 Median and range in values of field parameters, and concentrations of major ions, nutrients, and selected

 trace elements in ground-water and surface-water samples, by site, December 1996 and May 1998

[Concentrations are in milligrams per liter except where noted; n, number of samples; n = 23, except as shown; °C, degrees Celsius]

	Site 1 (n=7)	Site 2 (n=18)	Site 3 (n=9)	Site 4 (n=14)	Site 5 (n=20)	Site 6 (n=6)	Reference Site (n=12)	Citrus Sites (n=74)
	()	((0)	(,	(0)	(()	(
Temperature °C Median Range n	23.7 23.2-26.6	23.9 16.8-29.3 n=23	23.8 20.5-24.3 n=7	24.0 17.7-28.2 n=15	23.4 16.2-31.2 n=24	24.0 19.5-24.3 n=7	24.4 22.0-28.0 n=15	23.8 16.2-31.2 n=82
pH Median Range n	6.7 4.7-7.0	7.1 4.1-7.6 n=22	6.9 6.8-7.8	7.0 6.5-7.2 n=15	6.0 3.9-7.6 n=24	7.0 6.9-8.4 n=7	5.6 3.6-7.2 n=16	7.0 3.89-8.4 n=85
Dissolved solids (DS) Median Range n	1,360 1,020-1,980	749 298-1,370	1,190 732-2,060	796 462-1260	514 294-1,540	604 522-1,020	171 80.0-366	779 294-2060
Dissolved oxygen (DO) Median Range n	0.8 0.6-0.9	0.9 <0.1-4.5	1.2 <0.1-3.0 n=6	0.9 0.6-7.3 n=12	0.9 <0.1-7.2 n=23	0.7 0.5-5.6 n=5	0.7 0.3-5.6 n=15	0.9 <0.1-7.3 n=68
Calcium (Ca) Median Range n	150 84-280	120 42-250	160 74-290	155 51-260	52.5 24.0-200	150 84.0-200	11.6 0.9-71	115 24-290
Magnesium (Mg) Median Range n	57 6.0-100	18 10-26	33 11-73	18 11-27	15.5 8.0-44.0	12 4.0-42.0	2.7 0.6-5.0	18 4-100
Sodium (Na) Median Range n	160 67-260	59 6.9-88	150 58-400	71.5 30-130	53.0 29.0-150	31.5 13.0-60	15 7.4-29.0	65 6.9-400
Potassium (K) Median Range n	8.2 0.9-69	8.7 0.6-26	12 1.4-17	7.0 1.3-16	4.8 0.6-24.0	3.0 1.6-18	0.8 0.2-1.0	7.5 0.6-69
Chloride (Cl) Median Range n	540 290-580	130 19-250	420 130-580	110 35-240	110 54.0-470	76.0 26.0-110	22.5 13.0-61.0	125 19-960
Sulfate (SO ₄) Median Range n	210 150-530	210 81-380	120 77-310	260 41-430	120 3.9-340	85.0 30.0-280	4.6 0.2-13.0	160 3.9-530
Bicarbonate (HCO ₃) Median Range n	168 5.2-302	191 1.5-417	368 130-500	280 112-405	25.6 1.2-254	351 156-414	31.7 1.2-240	198 1.2-500 n=81

²² Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, Florida

Table 7. Median and range in values of field parameters, and concentrations of major ions, nutrients, and selected trace elements in ground-water and surface-water samples, by site, December 1996 and May 1998 (Continued)

[Concentrations are in milligrams per liter except where noted; n, number of samples; n = 23, except as shown; °C, degrees Celsius]

	Site 1 (n=7)	Site 2 (n=18)	Site 3 (n=9)	Site 4 (n=14)	Site 5 (n=20)	Site 6 (n=6)	Reference Site (n=12)	Citrus Sites (n=74)
Iron (Fe) μg/L Median Range n	2,600 20-89,000	1,400 20-8,700	400 <3-7,300	315 5-19,000	4,550 9.0-47,000	2,100 10.0-7,000	2,850 110-5,500	1750 <3.0-89,000
Manganese (Mn) μg/L Median Range n	37 <0.3-480	230 8.2-540	49 10-490	61.5 6.9-240	27.0 <0.3-110	26.5 4.3-150	8.0 2.6-56	40 <0.3-540
Silica (Si) Median Range n	17 7.3-40	11.5 9-20	14 10-17	12.5 5.3-18	11.5 0.4-26	14.5 4.8-18.0	9.4 7.4-18.0	12 0.4-40
Bromide (Br) Median Range n	1.3 0.83-2	0.44 0.09-0.8	1.4 0.48-3.4	0.39 0.14-0.9	0.35 0.1-1.6	0.3 0.14-0.44	0.1 0.05-0.2	0.45 0.09-3.4
Fluoride (Fl) Median Range n	0.2 <0.1-0.6	0.41 0.19-0.6	0.5 0.4-1.1	0.5 0.2-0.7	0.25 <0.1-0.5	0.4 0.2-0.5	<0.1 <0.1-0.2	0.4 <0.1-1.1
Nitrate (NO ₃) as N Median Range n	0.06 <0.02-13.9	<0.02 <0.02-26.0 n=25	<0.02 <0.02-<0.02	<0.02 <0.02-1.4	<0.02 <0.02-31 n=26	<0.02 <0.02-17.9 n=7	<0.02 <0.02-0.13 n=17	<0.02 <0.02-31 n=88
Ammonia (NH ₄) as N Median Range n	0.4 0.19-4.4	0.36 <0.01-6.2 n=25	0.07 <0.01-0.84	0.06 <0.01-1.0	0.71 <0.01-6.7 n=26	0.67 <0.01-1.2 n=7	0.18 <0.01-0.54 n=17	0.58 <0.1-6.7 n=78
Organic nitrogen Median Range n	0.35 <0.1-0.9	0.82 0.55-2.79 n=25	0.31 0.03-0.7	0.52 0.29-0.94	0.7 0.27-1.8 n=26	0.8 0.54-1.1 n=7	0.54 0.11-1.31 n=17	0.68 <0.1-2.79 n=78
Orthophosphate (PO ₄) as P Median Range n	<0.01 <0.01-<0.01	<0.01 <0.01-0.14 n=25	0.04 <0.01-0.21	<0.01 <0.01-0.22	<0.01 <0.01-0.08 n=26	<0.01 <0.01-0.04 n=7	0.02 <0.01-0.19 n=17	<0.01 <0.01-0.22 n=88
Phosphorus (P) total as P Median Range n	0.02 0.02-0.02	0.02 0.02-0.36 n=25	0.04 0.02-0.33	0.02 0.02-0.25	0.02 0.02-0.14 n=26	0.02 0.02-0.04 n=7	0.02 <0.01-0.23 n=17	<0.02 <0.02-0.36 n=88
Dissolved organic carbon (D Median Range n	OC) 39 12-79	17.5 8.4-55	66 33-95	35 3.7-77	20.5 10.0-78	21 7.7-79 n=7	46.0 13.0-79.0	25.5 3.7-9 n=72
Arsenic (As) µg/L Median Range n	<1 <1-16	1.4 <1-2.8 n=9	<1 <1-16 n=10	1.5 <1-5.5 n=7	1.65 <1.0-11 n=10	1.6 <1.0-6.6 n=7	2.4 <1.0-9.8 n=6	1.35 <1-16 n=50
Cadmium (Cd) µg/L Median Range n	<0.5 <0.5-7.0	<0.5 <0.5-0.7 n=9	<0.5 <0.5-0.7 n=10	<0.5 <0.5-1.1 n=7	<0.5 <0.5-3.3 n=10	<0.5 <0.5-<0.5 n=7	<0.5 <0.5-<0.5 n=6	<0.5 <0.5-7.0 n=50
Copper (Cu) µg/L Median Range n	<1 <1-1.5	<1 <1-12.0 n=9	<1 <1-2.7 n=10	<1 <1-2.6 n=7	1.1 <1.0-11.0 n=10	<1.0 <1.0-3.2 n=7	1.25 <1.0-10.0 n=6	<1.0 <1.0-12.0 n=50
Zinc (Zn) Median Range n	1.9 <1-61	4.8 <1-150 n=9	6.2 1.5-15 n=10	3.6 1.2-10 n=7	9.0 2.0-44 n=10	2.9 1.6-15 n=7	3.55 <1.0-13.0 n=6	4.7 <1.0-150 n=50

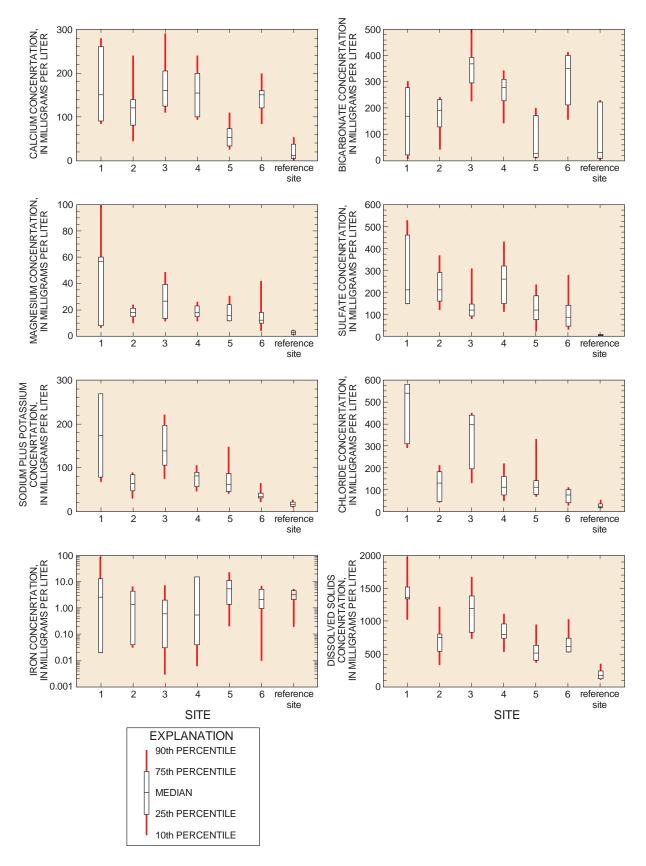


Figure 12. Major ions and nutrients at study sites, December 1996 and May 1998, Indian River, Martin, and St. Lucie Counties, Fla.

Table 8. Median and range in values of field parameters, and concentrations ofmajor ions, nutrients, and selected trace elements, by depth, at citrus sites,December 1996 and May 1998

[Concentrations are in milligrams per liter except where noted; n, number of samples; n=23, except as shown; $^{\circ}C$, degrees Celsius]

	Deep (n=23)	Midlevel (n=22)	Shallow (n=12)	Furrow (n=10)	Surface water (n=15)
Temperature °C Median Range n	24 23.0-25.5 n=25	24.1 21.4-26.6 n=24	23.0 20.5-26.8 n=14	23.5 20.5-27.0 n=11	23.7 16.2-31.2 n=17
pH Median Range n	7.0 6.7-7.2 n=25	6.9 4.7-7.4 n=23	6.2 4.1-7.8 n=16	6.6 3.9-7.5 n=11	7.2 6.2-8.4 n=17
Dissolved solids (DS) Median Range n	800 464-1,670	789 526-1,540	725 298-1,980	614 410-1,340	792 294-1,340
Dissolved oxygen (DO) Median Range n	0.5 0.4-1.0	0.9 0.3-2.4 n=21	1.4 0.06-3.7 n=8	0.9 <0.1-2.2 n=11	1.9 <0.1-7.3 n=17
Calcium (Ca) Median Range n	160 72.0-290	140 44.0-260	69.0 24.0-200	90.5 25.0-200	91.0 25.0-130
Magnesium (Mg) Median Range n	14 4.0-33.0	22.0 10.0-57.0	16.0 10.0-100	17.5 10.0-49.0	18.0 11.0-60.0
Sodium (Na) Median Range n	62.0 19.0-180	58.0 13.0-160	50.0 6.9-190	45.5 31.0-110	79.0 29.0-260
Potassium (K) Median Range n	1.3 0.6-7.4	14.0 1.6-25.0	14.0 3.3-69.0	8.35 3.1-24.0	5.5 2.2-11.0
Chloride (Cl) Median Range n	120 26.0-430	140 41.0-540	110 19.0-540	110 39.0-370	170 54.0-580
Sulfate (SO ₄) Median Range n	210 19.0-380	245 46.0-460	225 81.0-530	155 77.0-340	120 3.9-200
Bicarbonate (HCO ₃) Median Range n	238 190-415	179 5.2-405	40.2 1.2-415 n=13	146 8.2-500 n=11	212 36.6-254 n=16
Iron (Fe) µg/L Median Range n	6,900 1,500-23,000	2,520 6.0-89,000	375 <3.0-47,000	3,500 200-11,088	40.0 10-1,400
Manganese (Mn) µg/L Median Range n	49.0 16.0-150	59.0 0.3-340	61.0 26.0-540	128 9.3-490	12.0 <3.0-56.0
Silica (Si) Median Range n	13.0 10.0-18.0	9.9 5.4-26.0	13.5 7.7-40.0	14.0 11.0-25.0	9.1 0.4-17.0
Bromide (Br) Median Range n	0.4 0.14-1.4	0.4 0.1-1.6	0.36 0.09-1.3	0.42 0.2-1.0	0.53 0.15-2.0

Table 8. Median and range in values of field parameters, and concentrations ofmajor ions, nutrients, and selected trace elements, by depth, at citrus sites,December 1996 and May 1998 (Continued)

[Concentrations are in milligrams per liter except where noted; n, number of samples; n=23, except as shown; $^{\circ}C$, degrees Celsius]

	Deep (n=23)	Midlevel (n=22)	Shallow (n=12)	Furrow (n=10)	Surface water (n=15)
Fluoride (Fl)					
Median	0.3	0.28	0.50	0.4	0.4
Range	0.16-0.7	< 0.1-0.8	<0.1-0.8	< 0.1-1.1	0.22-0.60
n					
Nitrate (NO ₃) as N					
Median	< 0.02	0.22	1.8	< 0.02	< 0.02
Range	< 0.02-0.03	< 0.02-4.9	< 0.02-26.0	< 0.02-31.0	< 0.02-0.08
n	n=26	n=24	n=16	n=12	n=17
Ammonia (NH ₄) as N					
Median	0.61	0.38	0.7	0.54	0.03
Range	0.08-1.1	< 0.01-4.4	< 0.01-6.2	0.09-6.7	< 0.01-0.40
n	n=26	n=24	n=16	n=12	n=17
Organic nitrogen					
Median	0.38	0.66	0.85	0.88	0.76
Range	0.22-1.12	<0.1-1.0	0.31-2.79	0.3-2.6	0.18-1.83
n	n=26	n=24	n=16	n=12	n=17
Orthophosphate (PO ₄) as P					
Median	< 0.01	< 0.01	< 0.01	< 0.01	0.02
Range	< 0.01-0.08	< 0.01-0.1	< 0.01-0.08	<0.01-0.1	< 0.01-0.22
	n=26	n=24	n=16	n=12	n=17
Phosphorus (P) total as P Median					0.02
Range	< 0.02	< 0.02	< 0.02	< 0.02	0.03
U	<0.02-0.36	<0.02-0.12	<0.02-0.11	<0.02-33.0	<0.02-0.25
n Dissolved ereceric control (DC	n=26	n=24	n=16	n=12	n=17
Dissolved organic carbon (DC Median	· · ·	17.0	16.0	24.5	26.0
Range	21.0	17.0	16.0	24.5	36.0
n	3.7-79.0	5.7-77.0	7.7-67.0	11.0-95.0	12.0-79.0
Arsenic (As) µg/L		n=21	n=13		
Median	1.0	1.0	1.45	2.1	<1.0
Range	0.44-3.1	0.49-6.6	1.0-5.1	<1.0-16.0	<1.0-2.0
n	n=12	n=12	n=8	n=7	n=10
Cadmium (Cd) µg/L					
Median	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Range	<0.5-1.1	< 0.5-7.0	< 0.5-3.3	< 0.5-0.8	<0.5-<0.5
n	n=12	n=12	n=8	n=7	n=10
Copper (Cu) µg/L Median	<1.0	<1.0	2.55	<1.0	2.45
Range	<1.0-2.2	<1.0-3.2	<1.0-12.0	<1.0-4.0	<1.0-11.0
n	<1.0-2.2 n=12	<1.0-3.2 n=12	<1.0-12.0 n=8	<1.0-4.0 n=7	< 1.0-11.0 n=10
Zinc (Zn)	11-12	11-12	11-0	11-7	11-10
Median	1.65	3.85	14	6.8	10.45
Range	<1.0-15.0	1.4-61	1.9-150	2.2 12.0	1.9-44.0
n	<1.0-13.0 n=12	n=12	n=8	2.2 12.0 n=7	n=10

Concentrations of SO₄ in ground water were high at the citrus sites (median 160 mg/L) in contrast to the reference site (median 4.6 mg/L and maximum 13 mg/L), thus suggesting that there were few natural sources of SO₄ (fig. 12; tables 7, 8, and 9). High SO₄ concentrations in ground water from midlevel and deep wells at citrus sites were not expected because reducing conditions were indicated by low DO, high Mn and Fe concentrations, and the presence of sulfide and methane (table 10). Sulfate contributions from fertilizer can be substantial, but other oxidized species in fertilizers, such as NO₃, were not detected or were detected in much lower concentrations in deep and midlevel wells at citrus sites. Sulfate is a byproduct of a denitrification reaction involving the mineral pyrite (FeS₂), and can form in recent sediments rich in organic matter (Postma and others, 1991). Fertilizer as a source of SO₄ at citrus sites was indicated by significant positive correlations (p-values less than 0.05) between concentrations of SO₄ and concentrations of K, Cl, Ca, Mg, NH₄, Mn, NO₃ (other common components of fertilizer, potash, or liming agents).

Table 9. Median and range in values of field parameters, andconcentrations of major ions, nutrients, and selected trace elements,by depth, at the reference site, December 1996 and May 1998

[Concentrations are in milligrams per liter except where noted; n, number of samples; n=23, except as shown; $^{\circ}C$, degrees Celsius]

	Deep (n=3)	Midlevel (n=5)	Shallow (n=4)	Surface water (n=2)
				()
Temperature °C Median Range n	23.9 23.7-24.2 n=4	24.5 24.0-26.3 n=6	23.8 22.0-27.6 n=5	27.5 27.0-28.0
pH Median Range n	6.8 6.7-6.8 n=4	5.4 5.0-5.4 n=6	4.0 3.6-5.9 n=5	7.1 7.1-7.2 n=3
Dissolved solids (DS) Median Range n	240 214-240	156 128-350	114 80-126	276 186-366
Dissolved oxygen (DO) Median Range n	0.4 0.4-0.6 n=4	0.7 0.4-1.0 n=6	1.0 0.8-1.5	5.6 0.3-5.6 n=3
Calcium (Ca) Median Range n	54.0 47.0-54.0	8.2 5.5-21.0	2. 0.9-8.0	49.5 28.0-71.0
Magnesium (Mg) Median Range n	4.1 3.0-4.1	2.4 2.0-5.0	1.0 0.6-1.2	4.3 3.6-5.0
Sodium (Na) Median Range n	18.0 18.0-21.0	15.0 11.0-26.0	9.6 7.4-13.0	22.0 15.0-29.0
Potassium (K) Median Range n	0.8 0.7-0.8	0.9 0.8-0.9	0.5 0.2-1.0	0.7 0.4-1.0
Chloride (Cl) Median Range n	20.0 16.0-20.0	26.0 21.0-61.0	16.5 13.0-26.0	39.0 24.0-54.0
Sulfate (SO ₄) Median Range n	0.2 0.2-0.9	4.3 4.3-6.6	6.3 1.8-8.1	9.5 6.0-13.0
Bicarbonate (HCO ₃) Median Range n	213 200-239 n=4	20.7 11.2-46.3	4.4 1.2-87.0	224 96.3-229
Iron (Fe) µg/L Median Range n	5,500 3,700-5,500	3,200 2,400-4,600	2,300 1,800-5,300	150 110-190
Manganese (Mn) µg/L Median Range n	9.2 7.1-9.2	8.3 7.7-11.0	13.6 3.7-56.0	3.6 2.6-4.5
Silica (Si) Median Range n	11.0 11.0-13.0	10.0 8.2-18.0	7.9 7.4-8.7	9.1 8.2-10.0
Bromide (Br) Median Range n	0.1 0.1-0.1	0.1 0.1- 0.2	0.08 0.05-0.1	0.12 0.09-0.15
Fluoride (Fl) Median Range n	0.17 0.17-0.2	<0.1 <0.1-<0.1	<0.1 <0.1-<0.1	0.19 0.18-0.2

Table 9. Median and range in values of field parameters, and concentrations of major ions, nutrients, and selected trace elements, by depth, at the reference site, December 1996 and May 1998 (Continued)

[Concentrations are in milligrams per liter except where noted; n, number of samples; n=23, except as shown; °C, degrees Celsius]

	Deep (n=3)	Midlevel (n=5)	Shallow (n=4)	Surface water (n=2)
Nitrate (NO3) as N				
Median	< 0.02	< 0.02	< 0.02	0.04
Range	<0.02-<0.02	<0.02-<0.02	<0.02-0.1	< 0.02-0.13
n i AHLA M	n=4	n=6	n=5	n=3
Ammonia (NH ₄) as N	0.51	0.22	0.06	0.02
Median Range	0.51	0.22 0.18-0.31	0.06	<0.02
n	n=4	n=6	n=5	n=3
Organic nitrogen	11-4	n=0	11-5	n=5
Median	0.28	0.75	0.59	0.51
Range	0.21-0.35	0.54-1.28	0.45-1.31	0.48-0.56
n	n=4	n=6	n=5	n=3
Orthophosphate (PO ₄) as P				
Median	0.18	0.02	0.05	< 0.01
Range	0.15-0.19	0.02-0.04	< 0.01-0.15	<0.01-<0.01
	n=4	n=6	n=5	n=3
Phosphorus (P) total as P Median	0.19	< 0.02	0.05	< 0.02
Range	0.19	<0.02	<0.03	<0.02
n	n=4	<0.02-<0.02 n=6	<0.02-0.3 n=5	n=3
Dissolved organic carbon (DO		11-0	11-5	11-5
Median	13.0	53.0	38.5	47.0
Range	13.0-52.0	28.0-79.0	18.0-60.0	21.0-73.0
n				
Arsenic (As) µg/L				
Median	0.58	0.78	2.4	<1
Range	0.56-9.8	0.56-4.1	1.4-3.4	
n Cadminum (Cd) us /I	n=3	n=4	n=2	n=1
Cadmium (Cd) µg/L Median	<0.5	< 0.5	<0.5	<0.5
Range	<0.5	<0.5	<0.5	<0.5
n	n=3	<0.5-<0.5 n=4	<0.5-<0.5	n=1
Copper (Cu) µg/L	n=5			
Median	<1.0	5.5	2.7	<1
Range	<1.0-<1.0	<1.0-10.0	1.5-3.9	
n	n=3	n=2	n=2	n=1
Zinc (Zn)				
Median	<1.0	5.1	8.1	2.4
Range	. 1	4.0-6.1	3.1-13.0	. 1
n	n=1	n=4	n=2	n=1

Iron concentrations were generally high in ground water, but were significantly higher (p-values less than 0.01) in samples from deep wells (tables 8 and 9). The overall median iron concentration in ground water was 1.75 mg/L at citrus sites and 2.85 mg/L at the reference site. Berndt and Katz (1992) reported that iron concentrations are generally high in ground water from the surficial aquifer system in Florida. Iron is released under reducing conditions in aquifers where materials are coated with iron hydroxides. Iron concentrations in canal samples were significantly lower than in ground water (tables 8 and 9; fig. 13). In samples from all wells, values of pH and concentrations of Ca, Fe, and HCO_3 increased with depth as indicated by significant positive correlations with depth (p-values of 0.01, <0.01, 0.03, and <0.01, respectively). Increases in concentration with depth were probably the result of increased mineral dissolution of aquifer materials (limestone) with depth. Significant negative correlations with depth, for concentrations of DO, K, Mn, and NO₃ were detected, (p-values of <0.01, <0.01, 0.02, and <0.01, respectively). Decreased concentrations of these constituents with depth were likely the result of biological activity, cation exchange, precipitation, tree uptake, or dilution.

Table 10. Dissolved gas concentrations in ground water and estimated excess N_2 , recharge temperature, and excess air from midlevel and deep wells, May 1998

[Concentrations are in milligrams per liter (mg/L); cc STP/L, cubic centimeter per liter standard temperature pressure per liter; NA, data not available; H_2S measured only once at each well]

Sample (site-well)	N ₂	Ar	02	CO2	CH₄	H₂S	Median estimated excess N ₂ (mg/L as N)	Median estimated recharge (degrees Celsius)	Median estimated excess air (cc STP/L)
Site 2 A10 A10	18.113 17.877	0.489 .489	0.062 .078	7.878 7.993	0.006 .004	0.013	6	22.8 22.8	-2.1 -2.1
A20 A20 B20 B20	18.983 16.868 17.532 17.420	.509 .471 .440 .439	.292 .104 .066 .065	33.911 28.948 20.225 20.367	.059 .072 .022 .021	.001 .022 	6 6 8 8	22.9 23.0 22.6 22.7	-0.9 -3.1 -5.2 -5.2
Site 4 A10 A10 B10 B10 A20 A20 B20 B20 B20	15.109 17.174 18.589 18.653 31.831 19.103 18.447 18.393	.539 .577 .563 .564 .723 .503 .539 .538	.062 .066 .066 .195 3.264 .235 .060 .065	117.138 124.274 34.380 33.915 59.679 50.407 35.309 34.038	.006 .006 .002 .002 .011 .012 .001 .001	.044 .001 .033 .001	0 0 2 2 6 6 3 3 3	22.8 22.4 23.7 23.7 23.0 23.0 22.8 22.7	0.9 2.9* 2.8 2.9 12 * -1.2 0.8 0.8
Site 5 A10 A10 B10 B10 A20 A20 B20 B20	19.154 19.258 23.009 17.453 16.438 16.505 15.657 15.497	.545 .545 .624 .522 .509 .510 .518 .514	.190 .198 .324 .288 1.665 1.666 2.106 2.134	46.918 47.215 19.660 15.758 22.815 22.015 31.666 31.275	.208 .222 .001 .381 2.793 2.781 3.536 3.640	.028 .028 .020 .019 	4 3 3 3 3 2 2	21.9 21.8 23.9 23.9 22.7 22.8 21.7 21.8	0.6 0.7 6.6* 0.5 -1.0 -0.9 -1.0 -1.2
Reference A10 A10 A20 A20	15.792 15.754 17.420 16.296	.557 .560 .581 .559	.089 .168 .539 .532	93.253 94.583 51.838 48.645	.045 .173 .761 .801	0.312 NA 	0 0 0 0	21.7 21.1 22.3 22.9	1.3 1.1 3.1 2.1

* Values are high as the result of air leaks in the laboratory.

Dissolved-solids and chloride concentrations at citrus sites were significantly higher than concentrations at the reference site (fig. 12). Water in the surficial aquifer system in Florida generally contains low DS (less than 500 mg/L) (Franks, 1982; Berndt and Katz, 1992). Dissolved-solids concentrations of ground water at citrus sites ranged from 294-2,060 mg/L with a median of 779 mg/L-more than four times the median concentration at the reference site (median of 171 mg/L) (table 7). The median chloride concentration in samples from the six citrus sites was 125 mg/L compared to 22.5 mg/L at the reference site. Dissolvedsolids concentrations in samples from citrus groves were positively correlated with concentrations of Cl, K, Mn, Ca, Mg, Si, Na, HCO₃, Br, SO₄, F, PO₄, and organic nitrogen (p-values less than 0.05). Three factors that may have contributed to the high DS and Cl concentrations in ground water at the citrus sites were:

(1) the high volume of irrigation water that was recirculated through canals and the aquifer; (2) the addition of at least 200 lbs/acre per year of fertilizer and liming agents (Sarooshi, and others, 1994; Tucker and others, 1995; Guazzelli and others, 1996); and (3) the use of water from the Upper Floridan aquifer as an irrigation source. The median concentration of DS in the Upper Floridan aquifer was about 2,500 mg/L in the area (Katz, 1992). Dissolved-solids concentrations were highest at sites 1 and 3 where sources of irrigation water included water from the Upper Floridan aquifer. A water sample collected in December 1996 from a well at site 3, which taps the Upper Floridan aquifer, had a dissolved-solids concentration of 960 mg/L. Leaking capped wells that tap the Floridan aquifer system also may have increased DS concentrations in the surficial aquifer in some groves (Schiner and others, 1988).

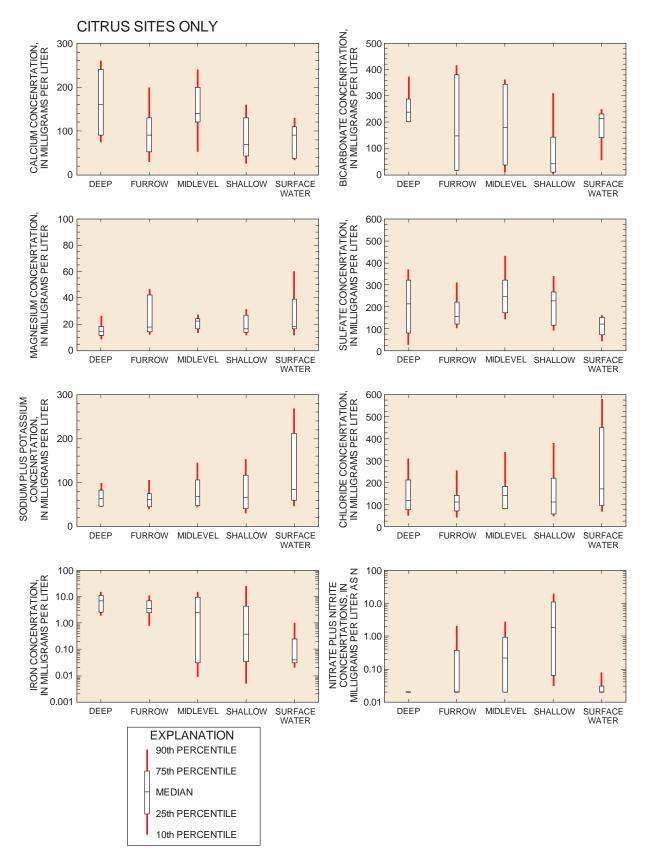


Figure 13. Major ions and nutrients at citrus sites, by depth, December 1996 and May 1998, Indian River, Martin, and St. Lucie Counties, Fla.

30 Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, Florida

The pH values were higher in ground water from shallow wells at the citrus sites (median of 6.2) than at the reference site (median of 4.0) (tables 8 and 9). High pH values, especially in shallow parts of the aquifer, are indicative of liming—the practice of applying calcium carbonate or dolomite to soils to raise the soil pH to optimal levels (6.0) for plant uptake of minerals and nutrients (Tucker and others, 1995). At all citrus sites, the median pH of water in the deep wells (7.0) was similar to the pH of the canal water (7.2) which suggests that, at least in part, water from deeper parts of the aquifer infiltrated upwards into the canals.

At all seven sites, DOC concentrations were high and DO concentrations were low. The median DOC concentration was 25.5 mg/L for samples from citrus sites and 46.0 mg/L for samples from the reference site. DOC concentrations in ground water are generally less than 2 mg/L (Thurman, 1985). DOC concentrations ranged from 3.7-95 mg/L and did not differ significantly by site (table 7) or depth (tables 8 and 9). DOC concentrations ranged from 13-79 mg/L at the reference site, indicating that DOC naturally occurred at high concentrations throughout the study area, most likely due to the decay of organic matter (table 9). The median DO concentration was 0.7 mg/L in ground water from the reference site and 0.9 mg/L in ground water from citrus sites, indicating suboxic or anoxic conditions. For instance, concentrations were lowest in the deep wells (medians ranged from 0.4-0.5 mg/L), progressively greater in the midlevel and furrow wells (medians ranged from 0.7-0.9 mg/L), and highest in the shallow wells (medians ranged from 1.0-1.4 mg/L) (tables 8 and 9). Dissolved oxygen concentrations were generally greater in the canal water than in ground water.

Trace Elements

Trace elements are a concern in water because high concentrations may harm fisheries and impair drinking water (U.S. Environmental Protection Agency, 1999). Trace element analyses were performed on water samples (table 11) to determine overall water-quality conditions at citrus sites and the reference site; Ba Cu, Zn, and Mo are applied as micronutrients in fertilizer, and As, Cd, and Se may be inadvertently included in sludge applied to citrus-production areas (Tucker and others, 1995). Concentrations of As, Be, Cd, Co, Cu, Mo, Se, Ag, and Zn in ground water from citrus sites were similar to those in samples from the reference site. At all sites, the maximum concentration of As at each site exceeded the recommended criteria for human consumption of 0.018 μ g/L (U.S. Environmental Protection Agency, 1999) and maximum concentrations of Cd at sites 1 and 5 exceeded the recommended continuous and maximum criteria for the health of aquatic organisms of 2.2 and 4.3 μ g/L, respectively (U.S. Environmental Protection Agency, 1999).

Table 11. Median trace-element concentrations, ranges,detection levels, and minimum percentage of samples belowdetection level in ground and surface water from all sites,December 1996

[Concentrations are in micrograms per liter; <, less than the detection level]

Constituent	Median	Range	Detec- tion level	Minimum percent- age below detection level
Ground Water (44 sam	ples)			
Arsenic (As)	<1	<1.0-16	<1	50
Aluminum (Al)	21	<3-1700	<3	5
Barium (Ba)	74	6-180	< 0.5	0
Beryllium (Be)	< 0.5	<0.5-0.7	< 0.5	95
Cadmium (Cd)	< 0.5	<0.5-7	< 0.5	50
Chromium (Ch)	<1.0	<1.0-4.3	<1.0	75
Cobalt (Co)	<1.0	<1.0-8.6	<1.0	50
Copper (Cu)	<1.0	<1.0-12	<1.0	50
Lead (Pb)	<1.0	<1.0-13	<1.0	75
Molybdenum (Mo)	2.75	<2-51	<2.0	25
Nickel (Ni)	2	<1.0-11	<1.0	10
Selenium (Se)	<1.0	<1.0-1.8	<1.0	50
Silver (Ag)	<1.0	<1.0-<1.0	<1.0	100
Zinc (Zn)	4.2	<1-150	<1.0	5
Surface Water (11 sam	ples)			
Arsenic (As)	<1	<1.0-2	<1	50
Aluminum (Al)	5	<3-350	<3	5
Barium (Ba)	43	13-63	< 0.5	0
Beryllium (Be)	<0.5	<0.5-<0.5	< 0.5	100
Cadmium (Cd)	<0.5	<0.5-<0.5	< 0.5	100
Chromium (Ch)	<1.0	<1.0-<1.0	<1.0	100
Cobalt (Co)	<1.0	<1.0-<1.0	<1.0	100
Copper (Cu)	2.3	<1.0-11	<1.0	25
Lead (Pb)	<1.0	<1.0-<0.1	<1.0	100
Molybdenum (Mo)	<2.0	<2.0-25	<2.0	50
Nickel (Ni)	1.1	<1.0-11	<1.0	25
Selenium (Se)	<1.0	<1.0-1.6	<1.0	50
Silver (Ag)	<1.0	<1.0-<1.0	<1.0	100
Zinc (Zn)	8.9	1.9-44	<1.0	0

Maximum concentrations of Al, and Zn also exceeded the continuous and maximum recommended criteria for aquatic life of 0.75 and 0.12 mg/L, respectively (U.S. Environmental Protection Agency, 1999). The maximum Cu concentrations in samples from sites 2, 5, and the reference site were very close to the recommended freshwater criteria of 13 µg/L (U.S. Environmental Protection Agency, 1999). Only concentrations of Al, Ba, Cr, Pb, and Ni differed significantly (p-values <0.05) between the reference site and the citrus sites. Of these constituents, only Ni concentrations were higher in ground water from citrus sites; Al, Cr, and Pb concentrations were higher in ground water from the reference site, indicating that these trace elements are derived from natural sources. Trace element occurrence, concentrations, and distributions are presented in table 11 and appendix II.

Nutrients

Nutrients discussed in this report include various nitrogen and phosphorus species. Several forms of nitrogen (NH_4 , NO_3 , and organic nitrogen) and phosphorus are applied annually to citrus trees to improve the growth of the trees and fruit production. Nitrogen in the form of NO_3 sometimes leaches into aquifers, impairing the use of ground water as a potable drinking-water source. Nitrate is known to cause "blue-baby syndrome" (methemoglobinemia), which can be a potentially lethal illness in small children. Nitrogen and phosphorus also produce algal blooms in surface water, and reduce oxygen availability to organisms.

Ammonium, Organic Nitrogen, and Phosphorus

Overall, concentrations of NH_4 , organic N, and phosphorus were fairly low in ground water and surface water. However, a few relatively high NH_4 concentrations (maximum of 6.7 mg/L) were found in samples from shallow wells and furrow wells at the citrus sites (table 8). Although concentrations of NH_4 from the reference site never exceeded 1.0 mg/L, they were not significantly lower than those from the citrus sites, indicating that there are natural sources of NH_4 . Concentrations of NH_4 were lowest in midlevel and furrow wells and highest in shallow and deep wells from the citrus sites (table 8). Only 5 percent of NH_4 concentrations in ground water were below the detection level of 0.01 mg/L; most concentrations were below the USEPA 1-hour, 3-year average aquatic criteria for NH_4 . Concentrations of NH_4 in canal samples also never exceeded the criteria.

Median concentrations of organic N were less than 1 mg/L in all samples. Concentrations of organic N were highest in samples from shallow, midlevel, and furrow wells and from site 2 (tables 7, 8, and 9). Urea, used in some fertilizer mixes, may account for these higher concentrations. Organic N also was relatively high in samples from the reference site (maximum of 1.31 mg/L), suggesting that organic nitrogen was naturally occurring in ground water in that area.

At least 50 percent of all sample concentrations of PO_4 and total P in ground water and surface water were below detection levels of 0.01 and 0.02 mg/L, respectively. Median concentrations of PO_4 and total P were equal to or less than 0.04 mg/L at all sites (table 7). Median concentrations of PO_4 and total P at the reference site were similar to those at the citrus sites, indicating natural sources (table 7). The carbonate material composing the aquifer at the level of the screened interval in the deep wells may have contained some phosphorus.

Nitrate

Concentrations of NO₃ in samples from shallow wells and some furrow wells at the citrus sites were substantially higher than NO₃ concentrations in ground water from deeper wells and from the reference site. Concentrations of NO₃ in samples from five shallow wells and furrow wells from sites 1, 2, 5, and 6 exceeded the USEPA MCL for NO3 in drinking water. The three highest NO₃ concentrations (all greater than 20 mg/L) at citrus sites were found in samples collected immediately following the highest fertilizer applications of the year. For example, 114 lbs/acre of nitrogen (in fertilizer) were applied as two applications in March and May 1997 at site 2; NO₃ concentrations in samples from the shallow wells and furrow wells collected in July 1997, exceeded 20 mg/L (table 8). Concentrations of NO₃ in ground water at the reference site never exceeded 0.1 mg/L. A seasonal increase in concentrations was detected in samples from midlevel wells in citrus areas only during spring and summer. Median NO₃ concentrations in samples from midlevel wells increased from below the detection level in December 1996 to 0.87 mg/L in samples collected in July 1997 and May 1998.

Concentrations of NO₃ were significantly correlated with K, DO, and SO₄ (p-values < 0.01), but no significant correlation was found between NO₃ concentrations and DS and Cl—both indicators of agricultural activity. Nitrate and K concentrations were significantly higher in samples from shallow and furrow wells at the citrus sites than in midlevel and deep wells, whereas DS and Cl concentrations were not statistically different by depth (table 8). If Cl was assumed to be a conservative tracer and indicator of agricultural activity, the presence of Cl in deeper wells and the lack of NO₃ and K in samples from midlevel and deep wells in citrus areas would indicate that NO₃ and K were not behaving in a conservative manner (fig. 14). Significant negative correlations (p-values < 0.05) were found between NO₃ and HCO₃ and Fe, which indicates that biological reactions may have been occurring in ground water (fig. 15).

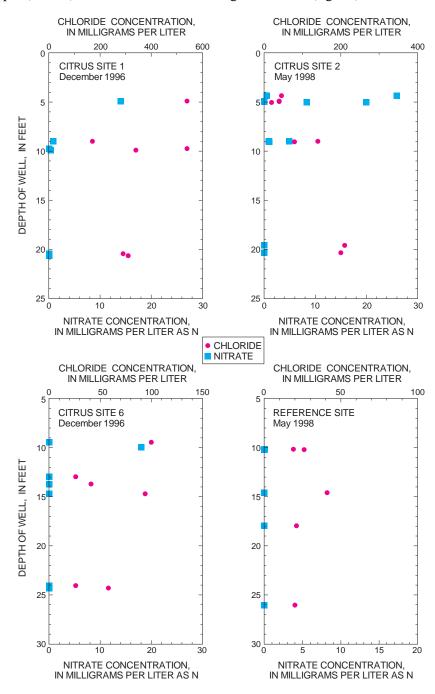


Figure 14. Chloride and nitrate concentrations compared by depth at sites 1, 2, 6, and the reference site.

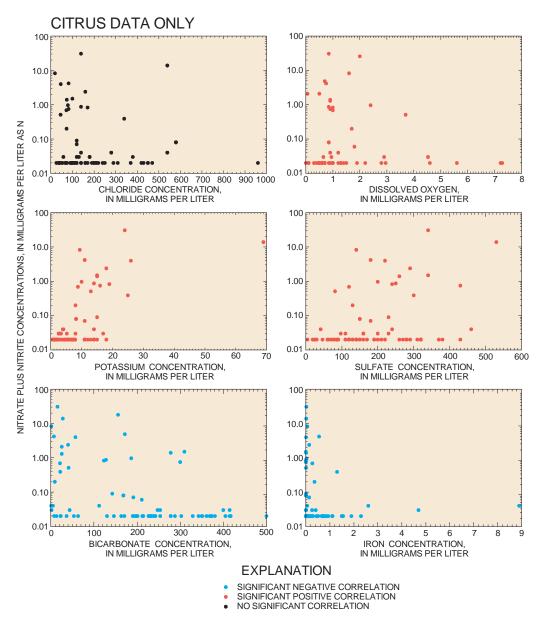


Figure 15. Correlations of nitrate concentrations with other constituent concentrations in samples from the citrus sites, Indian River, Martin, and St. Lucie Counties, Fla.

FATE OF NITRATE IN GROUND WATER

Any elevated NO_3 concentration in ground water is cause for concern because the surficial aquifer system supplies the majority of drinking water for Indian River, Martin, and St. Lucie Counties. About 24 percent (23 out of 95) of the samples collected from the citrus sites had NO_3 concentrations equal to or exceeding 0.2 mg/L, and only 5 percent (5 samples) had concentrations exceeding the USEPA MCL of 10 mg/L. Concentrations exceeded 10 mg/L in samples from shallow and furrow wells following heavy fertilizer applications. Several factors or processes may explain why NO₃ concentrations, which sometimes exceeded 20 mg/L in ground water at depths less than 7 ft, dropped to nearly zero at depths of about 20 ft. Possible explanations for the substantial decreases in NO₃ concentrations include dilution, tree uptake, movement off site, ammonification, and denitrification. Dilution probably contributed to reduced NO₃ concentrations in the midlevel wells. The vertical movement of water upward from the deep wells to the midlevel wells occurred, at least occasionally, at all of the sites except the reference site. The occurrence of high Cl and DS in samples from wells at

all depths indicates that dilution probably was not the dominant process responsible for the decrease in NO_3 with depth. Tree uptake of nitrogen primarily occurs above the water table; it is possible that when the water table rose in response to rainfall or irrigation, some nitrogen was removed from the ground water by tree uptake. The offsite movement of NO₃ was unlikely. Water-level data indicate that shallow ground water moved predominantly downward from the shallow wells and furrow wells; NO₃ concentrations in midlevel wells, deep wells, and in the canals (upgradient sites) were low or usually below detection levels. Ammonification also was not a likely process responsible for decreases in NO₂ concentrations, because the conversion of NO₃ to NH₄ generally preserves nitrogen in the system by increasing NH_4 concentrations; NH_4 concentrations remained less than 1 mg/L in most samples. Consequently, denitrification was probably the primary process responsible for the reduction in NO₃ concentrations with depth in the aquifer.

Geochemical factors required for denitrification to occur include: the presence of NO₃, denitrifying microbes, a suitable electron donor, and suboxic or anoxic (reduced) conditions (generally DO concentrations less than 2.0 mg/L) (Gillham, 1992; Korom, 1992). For substantial denitrification to occur, there must be adequate amounts of materials capable of electron (e) donation, such as organic carbon, pyrite, hydrogen sulfide, Mn, or Fe(II)-silicates (Postma and others, 1991). Organic carbon, if available, is thermodynamically favored to become the electron donor due to greater energy levels yielded by the reaction (Korom, 1991). Denitrification will proceed if the concentration of organic carbon equals or exceeds the concentration of NO₃ (Korom, 1992). The denitrification reaction in the presence of organic carbon is summarized as:

$$4NO_3^{-} + 5C^0 + 3H_2O = 2N_2 + 5HCO_3^{-} + H^+$$
 (2)

(Korom, 1992; Kendall and others, USGS, written commun., 1995). Note that N_2 and HCO₃ are products of the reaction. Denitrification reactions using pyrite (FeS₂) as the electron donor are also very common when organic carbon is not available. Denitrification using pyrite is summarized as:

$$5\text{FeS}_2 + 14\text{NO}_3^- + 4\text{H}^+ = 7\text{N}_2 + 10\text{SO}_4^{-2} + 5\text{Fe}^{2+} + 2\text{H}_2\text{O}$$
 (3)

(Postma and others, 1991). Note that N_2 , SO₄, and Fe are products of this reaction.

Conditions favorable for denitrification existed in ground water at each of the sites. Elevated concentrations of Fe and Mn, low DO concentrations, and the presence of CH_4 and sulfide indicate that reduced conditions were present in ground water. Concentrations of DOC and Fe were high in ground water throughout the study area, indicating that both organic carbon and pyrite were probably available as potential electron donors. Denitrification using organic carbon or pyrite would have resulted in increases in Fe, HCO₃ and SO_4 with depth, which is exactly what was observed at most sites. Quantifying denitrification using increases in these constituents was not possible because of the large amounts of SO₄ applied in fertilizers, HCO₃ from liming materials, and possible pyrite and carbonate dissolution in deep wells from aquifer materials. DOC concentrations were lower in samples from the midlevel wells than the shallow or deep wells, which may have been the result of consumption of organic carbon during denitrification reactions. Other evidence of denitrification came from measurements of nitrogen isotope ratios, δ^{15} N of NO₃ in ground water and measurements of N_2 gas.

Substantially enriched δ^{15} N values of NO₃ nitrogen were detected in samples from midlevel wells (median of +24.6 per mil) compared to those values observed in the shallow (median of +9.4 per mil) and furrow wells (median of +6.1 per mil) (fig. 16). Enrichment in δ ^{15}N values of NO_3 is produced by preferential uptake of the lighter ¹⁴N isotope and can indicate that denitrification occurs with depth. Values of δ^{15} N of NO₃ could not be determined for samples from deep wells or from the reference site because NO₃ concentrations were too low. Fertilizer samples collected from sites 2, 4, and 5 had a median δ^{15} N of NO₃ of +3.0 per mil with values ranging from +1.3 to +4.5 per mil. Enrichment in δ^{15} N in samples from midlevel wells agreed with water-level data, which indicated that water moved relatively rapidly from the shallow wells to furrow wells but more slowly to the midlevel wells. This relatively rapid movement of water in the shallow part of the aquifer reduced the amount of denitrification that may have occurred if the water had moved more slowly. Water movement from the shallow and furrow wells to the midlevel wells was much slower (vertical gradients were generally one order of magnitude lower), allowing time for more denitrification to occur.

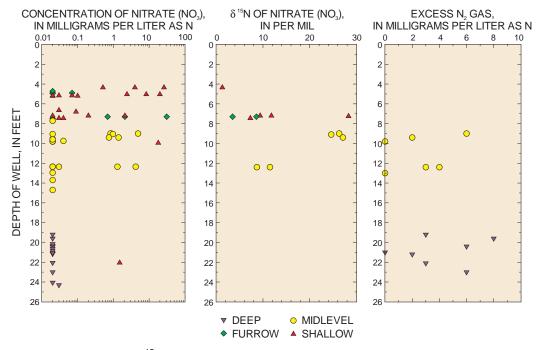


Figure 16. Nitrate, delta 15 N, and excess N₂ gas, by depth, at sites 2, 4, 5, and the reference site, July 1997 and May 1998.

An inverse relation was observed between δ^{15} N values of NO₃ and NO₃ concentrations (fig. 17) and may have been related to processes occurring along the ground-water flow paths. For example, the NO₃ concentration in water from a shallow well at site 2 was 26 mg/L and the δ ¹⁵N value was +1.3 per mil; however, the NO₃ concentration in water from a midlevel well at this same site was 0.87 mg/L and the δ^{15} N was +26.3 per mil from the deeper well at this site. The relation between NO₃ and δ^{15} N could be attributed to either: (1) two distinct sources of water, where one source is depleted in δ ^{15}N with high NO $_3$ concentrations and the other source is enriched in δ^{15} N with low NO₃ concentrations; or (2) denitrification and fractionation of the nitrogen isotopes of NO₃. Both processes likely occurred in ground water at the midlevel well depths, based on probable flow paths.

Values of δ^{15} N of NO₃ and NO₃ concentrations can be used to estimate enrichment factors (ϵ), which are useful to semiqualitatively compare denitrification rates in ground water. Mariotti and others (1988) found that for a single-step, nonreversible reaction, δ^{15} N increases proportionally with the logarithm of the residual NO₃ fraction according to the Rayleigh distillation equation. This equation is used to determine how the isotope ratio of a reactant changes as a reaction proceeds due to fractionation. The Rayleigh distillation equation (Mariotti and others, 1988) is:

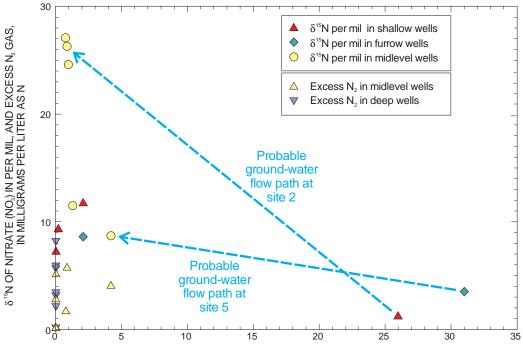
$$\delta^{15} N_i = \delta^{15} N_0 + \epsilon \ln C_i / C_0, \qquad (4)$$

where $\delta^{15}N_i$ is the concentration of $\delta^{15}N$ in the final reacted water, $\delta^{15}N_0$ is the $\delta^{15}N$ concentration of the initial source of nitrate, ϵ is the enrichment factor, ln is the natural log, and C_i/C_0 is the ratio of final NO₃ concentration to initial concentration. Enrichment factors in the range of -5 to -10 indicate rapid denitrification reactions (Mariotti and others, 1988).

Enrichment factors calculated for the study sites indicate that denitrification reactions not only occurred, but they occurred rapidly in the aquifer between the shallow and midlevel depths. For example, at site 2, ground water from shallow well A5 had a NO₃ concentration of 26 mg/L and a δ^{15} N value of +1.3 per mil (similar to that of fertilizer); ground water from midlevel well A10 had a NO₃ concentration of 0.87 mg/L and a δ^{15} N value of +26.3 per mil. The fact that the δ^{15} N values increased with depth and the NO₃ concentration occurred. The calculated enrichment factor (-7.4) indicates that denitrification occurred rapidly in ground water at site 2 (Mariotti and others, 1988).

The enrichment factor calculated for samples collected from site 5 at wells A5F and A10 was -6.0. These enrichment factors were similar to those found in the literature for ground water undergoing rapid denitrification (Cline and Kaplan, 1975; Wada and others, 1975; Black and Waring, 1977; Vogel and others, 1981; Mariotti and others, 1988; Bohlke and Denver, 1995).

Nitrogen gas is generated during denitrification reactions, thus, the presence of excess (above equilibrium concentrations) N_2 in ground water is an indication that denitrification has occurred. Results of analyses of N_2 and Ar gas concentrations can be used to estimate the concentrations of excess N_2 through an iterative trial and error approach. Equilibrium concentrations of Ar and N_2 exist in recharge water at specific temperatures at the time of recharge. Any excess N_2 in ground water at the time of sampling can be estimated by guessing N_2 concentrations until the recalculated values of recharge temperature are "reasonable," and there is good agreement between the two samples (samples were collected in duplicate) from each well (Heaton and Vogel, 1981). Reasonable values of ground-water recharge temperature are generally similar to the average annual temperature. Because the actual recharge temperature was not known at the sites, two bounds were placed on estimates of recharge temperature. First, the minimum recharge temperature was assumed to be 2.5 °C less than the field-measured ground-water temperatures, or roughly the average difference between recharge temperatures and groundwater field temperatures of samples with no excess N₂ (samples from the reference site and one sample from site 4). The minimum recharge temperature was similar to the annual average temperature. Second, the maximum recharge temperature was assumed to be equal to the measured ground-water field temperature. These two bounds on recharge temperature provided an upper and lower limit on the estimates of excess N_2 . Using minimum estimates of recharge temperature, maximum estimates of excess N₂ were calculated; using maximum estimated recharge temperatures, minimum estimates of excess N2 were calculated (L. Niel Plummer, U.S. Geological Survey, written commun., 1999).



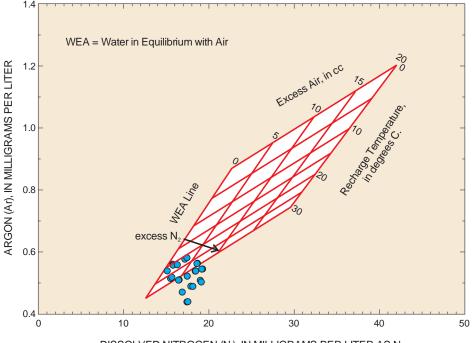
CONCENTRATION OF NITRATE (NO₃), IN MILLIGRAMS PER LITER AS N

Figure 17. Values of delta ¹⁵N of NO₃ and concentrations of excess N₂ gas compared to NO₃, sites 2, 4, and 5, July 1977 and May 1998.

Excess air concentrations also were calculated in the computation. Median values of estimated excess N₂, recharge temperature, and excess air were calculated from the maximum and minimum estimates, and the medians then were used as the final concentrations and temperatures for each sample (table 10). Differences in the estimated maximum and minimum excess N₂ concentrations from each sample were less than or equal to 1 mg/L. Three sample bottles had leaks in the laboratory, and so the values of excess air were not reliable; however, these samples were able to be used in calculations of excess N₂ and recharge temperature. A median recharge temperature of 22.8 °C and an excess air content of 0.6 cubic centimeters per liter (cm^3/L) at standard temperature and pressure conditions were calculated for all samples. The recharge temperature was in good agreement with the average annual air temperature for the study area (approximately 23 °C). The median excess air value was lower than atmospheric conditions $(2.0 \text{ cm}^3/\text{L})$ probably due to degassing (bubbling

out) at the water table due to the amount of the excess N_2 present. This supposition was supported by the many negative values of excess air.

Excess N₂ was measured in 10 of 13 samples collected (figs. 16 and 18). Median estimated excess N₂ concentrations ranged from 0-8 mg/L (figs. 16 and 18; table 10). The median excess N₂ of all samples was 3 mg/L. Estimated excess N_2 concentrations in samples from deep wells ranged from 0 (reference site, well A20) to 8 mg/L (site 2, well B20). The median and the maximum estimated excess N₂ in samples from deep wells (3 and 8 mg/L, respectively) was greater than the median and maximum concentrations in midlevel wells (2 and 6 mg/L, respectively), thus indicating that the highest rates of denitrification may have occurred in the zone between the midlevel and deep wells. Excess N₂ concentrations in samples from the reference site were 0 (table 10), which agreed well with the extremely low or nondetectable NO3 concentrations in ground water and indicated that denitrification was not occurring at the reference site.



DISSOLVED NITROGEN (N2), IN MILLIGRAMS PER LITER AS N

Figure 18. Concentrations of dissolved argon and N_2 in ground water compared to equilibrium concentrations of air in water at sites 2, 4, 5, and the reference site, May 1998.

SUMMARY

Water quality was analyzed at citrus groves in Indian River, Martin, and St. Lucie Counties, Florida, where the surficial aquifer system is the primary source of drinking water. Nitrate contamination of the surficial aquifer system is a concern in these three counties because of nitrogen in fertilizers, irrigation practices, sandy soils, high intensity rainfall events, and the proximity of the water table to the land surface. Six citrus grove sites in Indian River, Martin, and St. Lucie Counties and one reference site in St. Lucie County were selected to evaluate the distribution and the movement and fate of nitrate in ground water in citrus production areas. Groves were selected based on representative characteristics such as soil type, tree age, and management practices. Well arrangement in each grove consisted of eight wells in two clusters and one or two surface-water sites, depending on the pump and drainage canal arrangement. At the reference site, six wells were installed in two clusters in a layout similar to the citrus sites; one canal site was also established.

Wells and canals were sampled during one low fertilization period and during two high fertilization periods. Quality-assurance samples were also collected. Water samples were analyzed for field parameters, dissolved major ions, nutrients, trace elements, dissolved organic carbon (DOC), dissolved gases, isotopes of oxygen, hydrogen, nitrogen and carbon, tritium and tritogenic helium. The geochemical speciation program PHREEQC was used to calculate saturation indices and phase distribution. Water levels were measured monthly in most wells, twice monthly during peak fertilizer application periods, and quarterly in furrow wells and drainage canals. Pressure transducers, installed in the wells and the canal at site 2, measured relative water-level elevations in response to rainfall and irrigation from May 1998 through October 1998.

Water-level measurements and data from pressure transducers were used to establish patterns of ground-water flow to determine whether high NO₃ concentrations in shallow ground water were likely to affect the ground-water quality of the surficial aquifer system. Hydraulic gradients indicated that water moved rapidly from the shallow well depths downward to the deeper furrow wells. Deeper vertical circulation was much slower and more variable. The chemical composition of water in deep and midlevel wells was likely a mixture of deeper and shallower ground water (depending on canal levels and water levels in deeper parts of the aquifer). The δ ¹³C, calcite saturation indices, δ ¹⁸O, and δ D data also suggest that water in the midlevel wells may have been a mixture of water from deeper and shallower ground water. The age of water, determined by ³H/³He, was oldest in samples from deep wells at sites 5 (30-50 years) and 2 (20-23 years). The age of ground water from site 4 and the reference site was much younger (3-10 years).

Concentrations of the major and nutrient components of fertilizers, such as Cl, SO₄, NO₃, K, NH₄, and Mg, and some minor components such as Mn, were substantially higher in ground water from citrus sites than from the reference site. Mixed water types were the most common in samples from citrus sites, probably reflecting the contribution of irrigation water and the addition of fertilizers to the soil, thereby masking the natural water types. Dissolved-solids and chloride concentrations were high in ground water from the citrus sites compared with the reference site. DOC concentrations were high at every site. The median DOC concentration from citrus sites was 25.5 mg/L, which was relatively high for ground water. Reducing conditions also existed-DO concentrations were low throughout, and H₂S and CH₄ were detected at low levels. Trace element concentrations in ground water were generally low in the study area.

Concentrations of nutrients, NH_4 , organic N, PO₄, and total P, were relatively low in all samples. The median NH_4 concentration in samples from citrus sites was not substantially higher than those of the reference site. Median concentrations of organic N were less than 1 mg/L in all samples. At least 50 percent of all sample concentrations of PO₄ and total P in ground water and surface water were below detection levels of 0.01 and 0.02 mg/L, respectively.

Nitrate concentrations in samples from shallow and some furrow wells at the citrus sites were substantially higher than NO₃ concentrations in ground water from deeper wells at the citrus sites and ground water from the reference site. Samples from five shallow wells and furrow wells from sites 1, 2, 5, and 6 had NO₃ concentrations that exceeded the USEPA MCL of 10 mg/L for NO₃ in drinking water. The three highest NO₃ concentrations (all greater than 20 mg/L) occurred in samples collected in May 1998 or July 1997 from shallow or furrow wells at the citrus sites. Nitrate concentrations were substantially lower in samples from midlevel wells, deep wells, and canals. Nitrate concentrations in ground water were also significantly correlated with only two major components of fertilizer, K and SO_4 (p=<0.01), but no significant correlation was found between NO₃ concentrations and other prominent indicators of agricultural activity, such as dissolved solids and Cl.

Several processes may be occurring that would explain why NO₃ concentrations, which sometimes exceeded 30 mg/L in ground water at depths near 7 ft, dropped to near zero at depths of about 20 ft. Dilution probably played some role in the decrease in NO_3 ; the upward movement of water from deep wells to midlevel wells was documented at some sites. However, the absence of NO_3 and the relatively low NH_4 concentrations in samples from deep wells at the citrus sites indicated that denitrification probably was the main explanation for the decrease in NO₃. Conditions favoring denitrification were present in the aquiferlow DO and high DOC and Fe concentrations in ground water throughout the study area-both organic carbon and pyrite were probably available as potential electron donors. Higher δ^{15} N values were detected in samples from the midlevel wells than in samples from the shallow and furrow wells, thus indicating that denitrification was occurring and causing fractionation and enrichment. Excess N₂, found in 10 of 13 groundwater samples collected from midlevel and deep wells in May 1998, also indicated denitrification. Excess N₂ concentrations in samples from deep wells were typically greater than excess N₂ concentrations in samples from midlevel wells, indicating that higher rates of denitrification may have occurred in the zone between the midlevel and deep wells.

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APPENDIX I

ATTRIBUTES OF SAMPLING SITES IN THIS STUDY

Appendix I. Attributes of sampling sites in this study

[-, not applicable; relative elevation, northing and easting are based on an arbitrary datum at each site]

Sample identifier	Depth of sampling point (feet below land surface)	Sample Category	Screen length (feet)	Diameter of well (inches)	Relative elevation of measuring point (feet)	Relative northing coordinate (feet)	Relative easting coordinate (feet)
			Site 1				
A5	4.7	shallow well	2.5	1.5	100.21	10010.86	9766.65
A10	9.9	midlevel well	5	1.5	100.00	10010.58	9768.69
A20	20.65	deep well	2.5	1.5	100.30	10007.23	9770.72
A5F	4.7	furrow well	2.5	1.5	99.13	10019.82	9767.09
B20	20.45	deep well	2.5	1.5	99.71	10006.61	9929.24
B5	4.9	shallow well	2.5	1.5	99.43	10013.50	9930.00
B10	9.74	midlevel well	5	1.5	99.19	10011.78	9927.09
B5F	3.8	furrow well	2.5	1.5	96.94	10024.32	9928.78
S1	-	supply canal	-	-	-	-	-
82	-	drainage canal	-	-	85.20	10004.95	10015.17
			Site 2				
A5	4.35	shallow well	2.5	1.5	100.00	10262.35	9984.37
A10	9	midlevel well	2.5	1.5	100.00	10260.78	9984.71
A20	20.35	deep well	2.5	1.5	100.76	10258.85	9990.32
A5F	4.95	furrow well	2.5	1.5	98.99	10262.63	9975.28
B20	19.6	deep well	2.5	1.5	100.51	10042.86	9991.59
B5	5.04	shallow well	2.5	1.5	100.05	10046.02	9981.80
B10	9.05	midlevel well	2.5	1.5	99.93	10044.23	9982.03
B5F	4.9	furrow well	2.5	1.5	98.97	10043.05	9973.64
S1	-	supply/drainage canal	-	-	100.20	9984.10	9616.86
FERTILIZER	-	fertilizer sample	-	-	-	-	-
			Site 3				
A5	6.65	shallow well	2.5	1.5	100.07	9719.68	10012.90
A10	7.71	midlevel well	2.5	1.5	100.00	9717.70	10014.35
A20	20.86	deep well	2.5	1.5	99.98	9719.51	10006.97
A5F	4.92	furrow well	2.5	1.5	99.00	9717.32	10003.59
B20	20.15	deep well	2.5	1.5	99.60	9939.10	10008.26
B5	4.9	shallow well	2.5	1.4	99.92	9936.68	10015.95
B10	9.81	midlevel well	2.5	1.5	99.77	9937.63	10012.00
B5F	4.72	furrow well	2.5	1.5	99.02	9937.49	10005.12
S1	-	supply canal	-	-	-	-	-
82	-	drainage canal	-	-	100.79	10020.51	10017.60
FLORIDAN	-	Floridan well	-	-	-	-	-
			Site 4				
A5	6.8	shallow well	2.5	1.5	100.10	9794.04	9976.17
A10	9.8	midlevel well	5	1.5	100.00	9792.59	9976.25
A20	23	deep well	2.5	1.5	100.43	9793.24	9981.30
A5F	4.55	furrow well	2.5	1.5	98.13	9796.41	9964.21
B20	22.05	deep well	2.5	1.5	100.61	9948.29	9993.87
B5	7.25	shallow well	2.5	1.5	100.07	9946.81	9985.26

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Appendix I. Attributes of sampling sites in this study (Continued) [-, not applicable; relative elevation, northing and easting are based on an arbitrary datum at each site]

Sample identifier	Depth of sampling point (feet below land surface)	Sample Category	Screen length (feet)	Diameter of well (inches)	Relative elevation of measuring point (feet)	Relative northing coordinate (feet)	Relative easting coordinate (feet)
B10	9.4	midlevel well	5	1.5	99.81	9948.20	9986.41
B5F	4.65	furrow well	2.5	1.5	97.89	9949.26	9976.41
S 1	-	supply canal well	-	-	-	-	-
S2	-	drainage canal	-	-	101.08	10021.18	9816.74
FERTILIZER	-	fertilizer sample	-	-	-	-	-
			Site 5				
A5	7.2	shallow well	2.5	1.5	100.93	9813.16	9797.88
A10	12.35	midlevel well	2.5	2	100.04	9809.05	9796.40
A20	19.2	deep well	2.5	2	99.92	9809.17	9798.64
A5F	7.3	furrow well	2.5	2	100.00	9808.28	9793.81
B20	21.15	deep well	2.5	2	99.53	9811.42	9919.02
B5	7.45	shallow well	2.5	1.5	100.48	9816.34	9920.42
B10	12.35	midlevel well	2.5	2	99.63	9811.54	9916.74
B5F	7.5	furrow well	2.5	2	99.68	9810.97	9913.85
S1	-	supply canal	-	-	-	-	-
S2	-	drainage canal	-	-	83.56	10014.36	9988.36
MICROJET	-	micro-sprinkler sample	-	-	-	-	-
FERTILIZER	-	fertilizer sample	-	-	-	-	-
			Site 6				
A5	10.1	shallow well	2.5	1.5	101.03	9826.37	9852.64
A10	13.7	midlevel well	2.5	2	99.90	9825.08	9859.67
A20	24.3	deep well	2.5	2	100.00	9823.66	9858.51
A5F	9.55	furrow well	2.5	2	99.84	9826.88	9860.58
B20	24.05	deep well	2.5	2	100.08	9948.53	9864.23
В5	9.95	shallow well	2.5	1.5	101.06	9948.12	9858.03
B10	14.7	midlevel well	2.5	2	100.32	9944.01	9863.43
B5F	9.45	furrow well	2.5	2	99.96	9943.56	9865.14
S1	-	supply canal well	-	-	-	-	-
S2	-	drainage canal	-	-	81.86	10018.00	10016.44
		I	Reference	Site			
A5	5.16	shallow well	2.5	1.5	98.04	9829.70	9985.07
A10	12.96	midlevel well	2.5	2	100.47	9819.13	9994.85
A20	21.04	deep well	2.5	1.5	97.34	9821.93	9997.81
A13	13	test well well	2.5	2	100.00	9808.82	9989.91
B5	5.2	shallow well	2.5	1.5	97.79	9974.01	10009.15
B10	9.59	midlevel well	2.5	1.5	98.00	9963.60	10009.13
S1	-	drainage canal	-	-	91.39	10024.07	10003.84
RAINFALL		rainfall sample		_	,1.57	10021.07	10000101

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APPENDIX II

SAMPLING SCHEDULE OF CHEMICAL CONSTITUENTS, BY SITE

Appendix II. Sampling schedule of chemical constituents, by site

[1, sampling occurred in November-December 1996; 2, sampling occurred in July 1997; 3, sampling occurred in May-June 1998]

Sample identifier	Major ions	Nutrients	Dissolved organic carbon	Trace elements	15-nitrogen/	¹⁵ N/ ¹⁴ N of ammonia 15-nitrogen/ 14-nitrogen ratios	13-carbon/	¹⁸ O/ ¹⁶ O and D/P, 18-oxygen/ 16-oxygen ratios	Dissolved gases	³ H/ ³ He, Tritium/ helium ratios
					Site 1					
A5										
A10	1	1	1	1				1		
A20	1	1	1	1				1		
A5F										
B20	1	1	1	1				1		
B5	1	1	1	1				1		
B10	1	1	1	1				1		
B5F	1	1	1	1				1		
S1 S2	1 1	1 1	1	1 1				1		
52	1	1	1	1				1		
					Site 2					
A5	1,3	1,2,3	1,3	1	2,3	2,3	3	1,3	2	
A10	1,3	1,2,3	1,3	1	2,3	2,3	3	1,3	3	
A20	1,3	1,2,3	1,3	1	2,3	2,3	3	1,3	3	3
A5F B20	1,3 1,3	1,2,3 1,2,3	1,3 1,3	1 1	2,3 2,3	2,3 2,3	3 3	1,3 1,3	3	3
B20 B5	1,3	1,2,3	1,3	1	2,3	2,3	3	1,3	3	3
B10	1,3	1,2,3	1,3	1	2,3	2,3	3	1,3	3	
B5F	1,3	1,3	1,3	1	2,3	2,3	3	1,3	5	
S1	1,3	1,2,3	1,3	1	2,3	2,3	3	1,3		
FERTILIZER					3	3				
					Site 3					
A5	1	1	1	1				1		
A10	1	1	1	1				1		
A20	1	1	1	1				1		
A5F				1						
B20	1	1	1					1		
B5										
B10	1	1	1	1				1		
B5F	1	1	1	1				1		
S1 S2	1 1	1 1	1	1 1				1		
52 FLORIDAN	1	1	1	1				1		
LORIDAN		1	1	1	011- 4			1		
	_		â		Site 4			2		
A5	3	3	3					3		
A10	1,3	1,3	1,3	1	3	3	3	1,3	3	2
A20	1,3	1,3	1,3	1	3	3	3	1,3	3	3
A5F										2
B20	1,3	1,3	1,3	1	3	3	3	1,3	3	3
B5	1,3	1,3	1,3	1	3	3	3	1,3		
B10 B5F	1,3	1,3	1,3	1	3	3	3	1,3	3	
S 1	1,3	1,3	1,3	1		3	3	1,3		
S2	1,3	1,3	1,3	1		3	3	1,3		
FERTILIZER					3	3				

Appendix II. Sampling schedule of chemical constituents, by site (Continued) [1, sampling occurred in November-December 1996; 2, sampling occurred in July 1997; 3, sampling occurred in May-June 1998]

Site 5 A5 1.2.3 1.2.3 1.2.3 1.2.3 1.2.3 2.3 2.3 3 1.3 A10 1.2.3 1.2.3 1.2.3 1.2.3 2.3 3 1.3 3 A20 1.2.3 1.2.3 1.2.3 1.2.3 1.3 3 <t< th=""><th>Sample identifier</th><th>Major ions</th><th>Nutrients</th><th>Dissolved organic carbon</th><th>Trace elements</th><th>15-nitrogen/</th><th>¹⁵N/¹⁴N of ammonia 15-nitrogen/ 14-nitrogen ratios</th><th>13-carbon/</th><th>¹⁸O/¹⁶O and D/P, 18-oxygen/ 16-oxygen ratios</th><th>Dissolved gases</th><th>³H/³He, Tritium/ helium ratios</th></t<>	Sample identifier	Major ions	Nutrients	Dissolved organic carbon	Trace elements	15-nitrogen/	¹⁵ N/ ¹⁴ N of ammonia 15-nitrogen/ 14-nitrogen ratios	13-carbon/	¹⁸ O/ ¹⁶ O and D/P, 18-oxygen/ 16-oxygen ratios	Dissolved gases	³ H/ ³ He, Tritium/ helium ratios
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$											
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					1					3	3
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					1					3	3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1,3		1,3	1	3	3				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					1					3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	B5F	1,3	1,3	1,3	1	3	3	3	1,3		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1,3	1,2,3	1,3	1	3	3	3	1,3		
FERTILIZER 3 3 A5 - - A10 1 1 1 A20 1 1 1 A5F 1 1 1 B20 1 1 1 B5 1 1 1 B10 1 1 1 B11 1 1 1 B5 1 1 1 B10 1 1 1 B11 1 1 1 B5F 1 1 1 S1 1 1 1 S2 - - - Eference Site B5 1,3 A10 1,3 1,2,3 1,3 3 3 A20 1,3 1,2,3 1,3 3 3 3,3 A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,3 1 3 3		1,3	1,3	1,3	1	3	3	3	1,3		
Site 6 A5 1 1 1 1 A20 1 1 1 1 1 A5F 1 1 1 1 1 B20 1 1 1 1 1 B5 1 1 1 1 1 B5 1 1 1 1 1 B5F 1 1 1 1 1 B5F 1 1 1 1 1 B5F 1 1 1 1 1 S1 1 1 1 1 1 S2 2,3 2,3 3 1,3 A5 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,3 1 2,3 2,3 3 1,3 3 B5 1,3 1,3	MICROJET		3			3	3		3		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	FERTILIZER					3	3				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						Site 6					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A5										
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A10	1	1	1	1				1		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		1	1	1	1						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	A5F	1	1		1						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	B20	1	1	1	1				1		
B5F 1			1	1	1				1		
B5F 1		1									
S1 S2 1 1 1 1 1 Reference Site A5 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 3 B5 1,3 1,3 1,3 1 3 3 3 1,3 3 3 B10 1,3 1,2,3 1,3 1 3 3 3 1,3 3 3 1,3 3 3 S1 1,3 1,2,3 1,3 1 3 3 3 1,3 3 3			1	1							
S2 Reference Site A5 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 3 A13 1 2,3 1,3 3 3 1,3 3 3 B5 1,3 1,3 1 3 3 3 1,3 3 B10 1,3 1,3 1,3 1 3 3 1,3 3 S1 1,3 1,3 1 3 3 1,3 1 3 3 1,3			-								
A5 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 3 A13											
A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 3 A13						Reference Si	te				
A10 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 3 A13	A5	1.3	1.2.3	1.3	1	2.3	2.3	3	1.3		
A20 1,3 1,2,3 1,3 1 2,3 2,3 3 1,3 3 3 A13 <td></td> <td>,</td> <td></td> <td>·</td> <td></td> <td></td> <td></td> <td></td> <td>· ·</td> <td>3</td> <td></td>		,		·					· ·	3	
A13 B5 1,3 1,3 1,3 1 3 3 3 1,3 B10 1,3 1,3 1,3 1 3 3 3 1,3 3 S1 1,3 1,2,3 1,3 1 3 3 3 1,3 3						· ·					3
B5 1,3 1,3 1 3 3 3 1,3 B10 1,3 1,3 1 3 3 3 1,3 S1 1,3 1,2,3 1,3 1 3 3 3 1,3		1,5	1,2,5	1,0	•	2,0	2,0	0	1,5	5	5
B10 1,3 1,3 1 3 3 3 1,3 3 S1 1,3 1,2,3 1,3 1 3 3 3 1,3 3		13	13	13	1	3	3	3	13		
S1 1,3 1,2,3 1,3 1 3 3 3 1,3			· · · · ·							3	
										5	
RAINBALL 3 13	RAINFALL	1,5	3	1,5	1	5	5	5	1,3		

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APPENDIX III WATER-QUALITY DATA, 1996-98

					PH	PH			
					WATER	WATER	NITROGEN	NITROGEN	I NITROGEN
			SPECIFIC		WHOLE	WHOLE	AMMONIA	NITRITE	AMMONIA +
		TEMPER-	CON-	OXYGEN,	FIELD	LAB	DIS-	DIS-	ORGANIC
LOCAL		ATURE	DUCT-	DIS-	(STAND-	(STAND-	SOLVED	SOLVED	DISSOLVED
IDENTIFIER	DATE	WATER	ANCE	SOLVED	ARD	ARD	(MG/L	(MG/L	(MG/L
		(DEG°C)	$(\mu S/CM)$	(MG/L)	UNITS)	UNITS)	AS N)	AS N)	AS N)
ite 6									
10	12-19-96	24.	743.	0.6	7.01	7.33	.14	<.01	.93
20	12-19-96	23.3	963.	.65	6.99	7.87	.96	.03	1.5
20	12-18-96	24.1	780.	.5	6.96	7.12	1.1	<.01	2.2
5	12-18-96	24.3	878.		7.53		.67	.084	1.7
10	12-18-96	24.1	1087.	.7	6.93	7.12	1.2	<.01	2.
10	12-18-96	24.1	1087.	.7	6.93	7.21	1.2	<.01	1.7
5F	12-18-96	23.3	1315.		7.15	7.36	.26	<.01	1.2
L	12-13-96	19.5	876.	5.6	8.42	8.2	.01	<.01	.69
1	12-13-96	19.5	876.	5.6	8.42	8.18	.011	<.01	.71
L	12-19-96					5.63	<.01	<.01	<.2
			· — — -						
ite 5 ICROJET	05-14-98								
ICROJET	05-14-98						<.01	<.01	1.3
5		22.8	479.	1.2	5.9	5.89		.012	1.6
	12-17-96 07-14-97						.44		
-		24.5	643.	.06	5.72		1.2	.012	1.9
5	07-14-97	24.5	643.	.06	5.72		1.2	.011	2.1
5	05-20-98	22.9	585.	1.7	6.01	5.62	.73	<.01	1.9
10	12-17-96	22.5	785.	1.	5.87	5.52	1.1	.012	2.1
10	07-15-97	24.1	772.	.9	5.58		3.2	.012	3.7
LO	05-20-98	23.1	657.	.75	5.59	5.31	2.	.016	2.7
20	12-17-96	23.3	983.	.5	7.21	7.43	.76	<.01	1.2
20	07-14-97	23.4	1052.	.5	7.22		.93	<.01	1.2
20	05-20-98	24.	904.	. 4	7.03	7.32	.83	<.01	1.2
20	05-20-98					7.24	.83	<.01	.95
ōF	12-17-96	21.6	562.	1.	5.86	5.85	.09	.02	1.4
F	07-15-97	24.8	838.	.5	5.56		1.1	<.01	1.8
5F	05-20-98	25.1	1367.	.85	5.55	5.97	6.7	<.01	7.
20	12-16-96	23.7	798.	.5	6.96	7.19	.66	<.01	1.
20	05-14-98	23.	808.	.5	6.92	6.89	.68	<.01	1.
5	12-16-96		1649.		5.8	4.74	.91	.018	1.5
5	05-14-98	23.	1369.	1.2	4.73	4.16	.78	.013	1.3
.0	12-16-96	22.9	1916.	.3	10.48	9.31	1.4	.016	2.
LO	05-14-98	25.1	1008.	.95	6.67	6.68	.68	<.01	1.2
F	12-16-96	21.5	662.		3.89	5.64	.34	<.01	1.2
F	05-14-98	24.4	904.	.7	5.47	5.37	.35	<.01	.92
-	12-13-96	16.2	549.	4.6	7.23	7.23	.046	<.01	1.1
-	07-14-97	31.19	562.	7.22	7.28		.018	<.01	.89
L	05-21-98	26.5	614.	1.9	6.83	7.19	.034	<.01	1.1
2	12-13-96	16.5	412.	2.8	7.57	6.86	.018	<.01	.76
2	05-21-98	24.	574.	.0	6.23	6.89	.27	<.01	2.1
ERTILIZER	07-08-98								
te 4 ERTILIZER	07-08-98								
								<.01	.9
5	05-12-98	44.5	1109.		6.48	7.01	<.UI	<.UI	. 🤊

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		NITRO-		PHOS-					
		GEN,	PHOS-	PHORUS	CARBON,		MAGNE-		POTAS-
		NO2+NO3	PHORUS	ORTHO,		CALCIUM	SIUM,	SODIUM,	SIUM,
		DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L
		AS N)	AS P)	AS P)	AS C)	AS CA)	AS MG)	AS NA)	AS K)
ite 6									
10	12-19-96	<.02	.02	.02	21.	120.	10.	13.	18.
120	12-19-96	.03	.04	.01	21.	150.	12.	29.	2.9
320	12-18-96	<.02	.04	.01	25.	150.	4.	19.	1.8
5	12-18-96	18.	<.02	<.01	7.7				
10	12-18-96	<.02	.03	<.01	18.	160.	18.	34.	1.6
310	12-18-96	<.02	.03	<.01	17.	170.	19.	36.	1.7
5F	12-18-96	<.02	<.02	<.01	26.	200.	42.	39.	3.1
31	12-13-96	<.02	.04	<.01	79.	84.	12.	60.	4.4
31	12-13-96	<.02	.03	<.01	79.	87.	12.	57.	4.4
1	12-19-96	<.02	<.02	<.01	.8	.02	.004		<.1
		·			- — —				
te 5	05 14 00								
ICROJET	05-14-98								
ICROJET	05-14-98	<.02	.14	.08					
5	12-17-96	<.02	.02	.02	32.	24.	14.	34.	7.6
	07-14-97	2.1	.03	<.01					
	07-14-97	2.3	.02	<.01					
	05-20-98	.2	<.02	.01	19.	26.	13.	31.	8.
.0	12-17-96	<.02	.02	.01	27.	44.	24.	59.	11.
2	07-15-97	1.3	.02	<.01					
0	05-20-98	4.2	<.02	.01	17.	52.	24.	32.	11.
20 20	12-17-96	<.02	.05	.05	78.	72.	11.	96. 	3.2
	07-14-97 05-20-98	<.02 <.02	.04 <.02	.01		90.		62.	2.
0	05-20-98	<.U2 .03	<.02	.04	10. 11.	90. 87.	11.	62. 59.	2. 1.9
20 5F	05-20-98 12-17-96	.03	<.02 .02	.03	11. 30.	87. 34.	11.	59. 38.	8.8
5F	07-15-97	2.1	.02	.01 <.01			±/. 		
5F	07-13-97	31.	<.02	<.01	14.	130.	44.	49.	24.
20	12-16-96	<.02	.02	.08	72.	88.	8.	49. 46.	.8
20	05-14-98	<.02	.04	.03	12.	75.	11.	45.	.6
5	12-16-96	.03	.02	<.01	10.	62.	31.	150.	3.3
5	05-14-98	.04	<.02	<.01	10.	58.	30.	140.	4.1
10	12-16-96	<.02	.02	<.01	11.	200.	15.	150.	2.4
10	05-14-98	.03	<.02	.01	14.	67.	12.	110.	2.5
5F	12-16-96	<.02	.03	<.01	23.	25.	14.	64.	4.
5F	05-14-98	<.02	<.02	<.01	11.	53.	30.	68.	5.9
1	12-13-96	<.02	.06	<.01	31.	38.	16.	38.	7.9
1	07-14-97		.02	<.01					
1	05-21-98		<.02	.02	22.	34.	18.	48.	7.
2	12-13-96	.02	.03	<.01	33.	25.	11.	29.	5.4
2	05-21-98		.05	.05	36.	34.	17.	57.	2.2
ERTILIZER	07-08-98								
		· — — —							
te 4									
ERTILIZER -	07-08-98								
5	05-12-98	.09	.04	.04	13.	93.	16.	74.	15.

		CIUT O		ET IIO	011 103			DEDVI	
		CHLO- RIDE,	SULFATE	FLUO- RIDE,	SILICA, DIS-	ARSENIC	BARIUM,	BERYL- LIUM,	CADMIUM
		DIS-	DIS-	DIS-	SOLVED	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	(MG/L	SOLVED	SOLVED	SOLVED	SOLVED
DENTIFIER	DATE	(MG/L	(MG/L	(MG/L	AS	(µG/L	(µG/L	(µG/L	(µG/L
JENTIFIER	DATE	AS CL)	AS SO4)	AS F)	SIO2)	AS AS)	(µG/1 AS BA)	(µG/H AS BE)	AS CD)
е б		,	,			,	. ,		
6	12-19-96	41.	46.	. 2	7.5	2.2	38.	<.5	<.5
	12-19-96	58.	110.	.4	15.	1.6	42.	<.5	<.5
	12-18-96	26.	30.	.4	18.	1.6	44.	<.5	<.5
)	12-18-96					1.5	78.	<.5	<.5
	12-18-96	94.	140.	.5	15.	6.6	53.	<.5	<.5
	12-18-96	96.	140.	.5	15.	6.6	56.	<.5	<.5
,	12-18-96	100.	280.	.4	14.	3.6	140.	<.5	<.5
	12-13-96	110.	60.	.3	4.8	1.	30.	<.5	<.5
	12-13-96	110.	60.	.3	4.9	<1.	30.	<.5	<.5
	12-19-96	<.1	<.2	 <.1	.02	<1.	<.2	<.5	<.5
	<u> </u>		~.2		.02			· <u> </u>	
5									
OJET	05-14-98								
ROJET	05-14-98								
	12-17-96	67.	89.	.5	11.	1.1	37.	<.5	<.5
	07-14-97								
	07-14-97								
	05-20-98	73.	130.	.3	10.				
	12-17-96	110.	190.	.2	11.	<1.	88.	<.5	.8
	07-15-97								
	05-20-98	82.	180.	.18	9.8				
	12-17-96	140.	63.	.4	12.	3.1	35.	<.5	<.5
	07-14-97								
	05-20-98	120.	78.	.16	10.				
	05-20-98	120.	74.	.16	10.				
	12-17-96	72.	120.	.4	12.	<1.	53.	<.5	<.5
	07-15-97								
	05-20-98	140.	340.	.49	17.				
	12-16-96	110.	19.	.3	12.	1.8	33.	<.5	.6
	05-14-98	110.	24.	.2	13.				
	12-16-96	380.	230.	<.1	21.	5.1	140.	<.5	3.3
	05-14-98	280.	240.	.14	26.				
	12-16-96	470.	170.	.1	5.4	1.	180.	<.5	<.5
	05-14-98	180.	160.	.16	13.				
	12-16-96	120.	120.	<.1	18.	11.	46.	<.5	.8
	05-14-98	140.	220.	<.1	25.				
	12-13-96	68.	110.	.4	3.	2.	32.	<.5	<.5
	07-14-97								
	05-21-98	93.	90.	.38	.4				
	12-13-96	54.	70.	.3	6.4	1.5	24.	<.5	<.5
	05-21-98	90.	3.9	.36	3.6				
FILIZER	07-08-98								
4									
ILIZER	07-08-98								
	05-12-98	120.	230.	.49	12.				

54 Distribution, Movement, and Fate of Nitrate in the Surficial Aquifer Beneath Citrus Groves, Indian River, Martin, and St. Lucie Counties, Florida

		armo						MOLUD	
		CHRO-	00000	0000000	TROM	1	MANGA-	MOLYB-	NT 00000
		MIUM,	COBALT,	COPPER,	IRON,	LEAD,	NESE,	DENUM,	NICKEL,
		DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(µG/L	(µG/L	(µG/L	(µG/L	(µG/L	(µG/L	(µG/L	(µG/L
		AS CR)	AS CO)	AS CU)	AS FE)	AS PB)	AS MN)	AS MO)	AS NI)
ite 6									
10	12-19-96	<1.	1.1	3.2	940.	<1.	6.9	<2.	5.2
20	12-19-96	<1.	<1.	2.2	2600.	<1.	38.	4.	2.3
20	12-18-96	<1.	<1.	<1.	1600.	<1.	150.	<2.	1.
5	12-18-96	<1.	<1.	3.		<1.		4.2	1.9
LO	12-18-96	<1.	<1.	<1.	5000.	<1.	15.	2.4	5.
.0	12-18-96	<1.	<1.	<1.	5100.	<1.	15.	2.2	5.5
F	12-18-96	<1.	1.2	<1.	7000.	<1.	96.	4.7	6.2
	12-13-96	<1.	<1.	<1.	10.	<1.	4.3	<2.	1.1
	12-13-96	<1.	<1.	1.1	10.	<1.	4.3	<2.	1.6
	12-19-96	<1.	<1.	6.5	<1.	<1.	<.2	<2.	<1.
te 5									
CROJET	05-14-98								
CROJET	05-14-98								
	12-17-96	1.2	1.1	3.	5000.	<1.	26.	<2.	1.6
	07-14-97								
	07-14-97								
	05-20-98				3600.		37.		
	12-17-96	<1.	1.9	1.2	9400.	<1.	35.	<2.	2.4
	07-15-97								
	05-20-98				5500.		32.		
	12-17-96	<1.	<1.	<1.	1900.	<1.	97.	2.2	<1.
	07-14-97								
	05-20-98				6900.		110.		
	05-20-98				6500.		100.		
7	12-17-96	1.3	<1.	4.	2700.	<1.	22.	<2.	2.1
,	07-15-97								
r	05-20-98				200.		32.		
)	12-16-96	<1.	<1.	<1.	8200.	<1.	28.	<2.	<1.
)	05-14-98				23000.		19.		
	12-16-96	<1.	4.2	<1.	47000.	2.6	56.	<2.	3.7
	05-14-98				26040.		45.		
)	12-16-96	<1.	<1.	<1.	9.	<1.	.3	3.8	4.2
)	05-14-98				4100.		9.2		
F	12-16-96	<1.	2.8	<1.	11000.	<1.	9.3	3.1	1.9
F	05-14-98				11088.		12.		
	12-13-96	<1.	<1.	8.8	1400.	1.	12.	<2.	1.9
	07-14-97								
	05-21-98				250.		11.		
	12-13-96	<1.	<1.	11.	180.	<1.	12.	<2.	11.
	05-21-98				1000.		34.		
RTILIZER	07-08-98								
.e 4									
TILIZER	07-08-98								
	07-08-98				40.		27.		
5	05 12 70				10.		<i></i>		

						ALKA-	SOLIDS,		C-13/
				ALUM-	SELE-	LINITY	RESIDUE		C-12
		SILVER,	ZINC,	INUM,	NIUM,	WAT DIS	AT 180	BROMIDE	STABLE
		DIS-	DIS-	DIS-	DIS-	TOT IT	DEG. C	DIS-	ISOTOPE
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	FIELD	DIS-	SOLVED	RATIO
IDENTIFIER	DATE	(µG/L	$(\mu G/L$	(µG/L	$(\mu G/L$	MG/L AS	SOLVED	(MG/L	PER
		AS AG)	AS ZN)	AS AL)	AS SE)	CACO3	(MG/L)	AS BR)	MIL
Site 6									
A10	12-19-96	<1.	1.6	5.7	<1.	287.	526.	.28	
A20	12-19-96	<1.	1.7	8.2	<1.	328.	674.	.24	
B20	12-18-96	<1.	15.	23.	<1.	340.	522.	.14	
B5	12-18-96	<1.	4.1	3.3	<1.	128.			
B10	12-18-96	<1.	2.9	13.	<1.	288.	732.	.35	
B10	12-18-96	<1.	14.	17.	<1.	288.	734.	.35	
B5F	12-18-96	<1.	2.8	29.	<1.	312.	1020.	. 44	
S1	12-13-96	<1.	5.2	29. 5.	<1.	174.	534.	. 44	
S1	12-13-96	<1.	5.2	5. 4.8	<1.	174.	534.	. 32	
S1	12-13-96	<1.	3.3	<3.	<1.		12.	.32 <.1	
Site 5									
MICROJET	05-14-98								
MICROJET	05-14-98								
A5	12-17-96	<1.	10.	300.	<1.	18.6	364.	.26	
A5	07-14-97								
A5	07-14-97								
A5	05-20-98						402.	.3	-20.92
A10	12-17-96	<1.	9.5	250.	1.1	19.	554.	.33	
A10	07-15-97					21.			
A10	05-20-98						528.	.1	
A20	12-17-96	<1.	5.5	17.	<1.	208.	566.	.5	
A20	07-14-97					156.			
A20	05-20-98						540.	.4	-10.29
A20	05-20-98						520.	.6	
A5F	12-17-96	<1.	8.5	490.	<1.	17.6	430.	.23	
A5F	07-15-97					21.			
A5F	05-20-98						938.	. 2	-21.06
B20	12-16-96	<1.	2.	29.	<1.	186.	500.	.36	
B20	05-14-98						464.	.3	-8.55
в5	12-16-96	<1.	13.	260.	1.5		966.	1.3	
в5	05-14-98						834.	1.	-21.42
В10	12-16-96	<1.	2.5	11.	1.4	134.	1540.	1.6	
B10	05-14-98						656.	.8	-19.63
B5F	12-16-96	<1.	6.8	230.	<1.		450.	.5	
B5F	05-14-98						598.	.4	-22.17
S1	12-13-96	<1.	23.	350.	<1.	44.	376.	.18	
S1	07-14-97								
S1	05-21-98						404.	. 2	-10.24
S2	12-13-96	<1.	44.	140.	<1.	30.	294.	.15	
S2	05-21-98						380.	.5	-6.6
FERTILIZER	07-08-98								
					·			- — — ·	
Site 4									
FERTILIZER	07-08-98								
A5	05-12-98						718.	.5	

			0.10/			AT1 E (and 1	AT1 E (200 1	005	2270
		H-2/	0-18/				N15/N14		ANC
		H-1	0-16			NO3	NH4	CIFIC	UNFLTRD
		STABLE	STABLE		N15/N14		FRAC	CON-	TIT 4.5
		ISOTOPE	ISOTOPE	NO3	NH4	WATER	WATER	DUCT-	LAB
LOCAL		RATIO	RATIO	FRAC	FRAC	FLTRD	FLTRD	ANCE	(MG/L
IDENTIFIER	DATE	PER	PER	SOIL	SOIL	0.45 U	0.45 U	LAB	AS
		MIL	MIL	PER MIL	PER MIL	PER MIL	PER MIL	$(\mu S/CM)$	CACO3)
Site 6									
A10	12-19-96	-16.4	-3.45					744.	290.
420	12-19-96	-6.1	-1.9					934.	314.
320	12-18-96	-9.1	-2.5					772.	349.
35	12-18-96	-9.1	-2.4						
310	12-18-96	-6.3	-1.84					1050.	286.
310	12-18-96							1050.	286.
35F	12-18-96	-6.7	-1.98					1280.	309.
31	12-13-96	.6	48					833.	197.
31	12-13-96							833.	197.
1	12-19-96							1.2	4.2
		· — — -							
te 5									
ICROJET	05-14-98		.25						
ICROJET	05-14-98								
5	12-17-96	-18.7	-3.76					468.	16.
5	07-14-97					11.8	15.8		
	07-14-97								
i	05-20-98	-13.7	-3.			9.4	11.8	566.	7.8
0	12-17-96	-17.	-3.59					748.	8.3
.0	07-15-97					11.5	13.3		
0	05-20-98	-12.4	-3.03			8.7	16.3	708.	6.1
0	12-17-96	1.2	14					942.	201.
0	07-14-97								
20	05-20-98	-2.1	81				б.	844.	162.
0	05-20-98							837.	164.
F	12-17-96	-20.5	-4.08					552.	16.
F	07-15-97					8.6	17.5		
F	05-20-98	-12.1	-2.82			3.5	16.7	1330.	13.
20	12-16-96	7.	1.29					740.	189.
20	05-14-98	6.6	1.07				4.3	667.	165.
5	12-16-96	-14.5	-3.01					1620.	1.6
5	05-14-98		-2.54			7.3	9.4	1380.	<1.
LO	12-16-96	-7.2	-1.96					1920.	18.
10	05-14-98	-10.9	-2.57				5.6	1020.	36.
5F	12-16-96	-15.4	-3.12					639.	11.
5F	05-14-98	-11.6	-2.41				7.4	905.	6.7
1	12-13-96	-8.	-1.54					548.	41.
1	07-14-97								
L	05-21-98		2.27					616.	52.
2	12-13-96	-12.6	-2.98					407.	30.
2	05-21-98	-2.4	63				.4	578.	140.
ERTILIZER	07-08-98			1.3	7				
		. — — .							
te 4				2	_				
RTILIZER	07-08-98			3.	б				
	05-12-98	-10.6	-2.49					1100.	117.

					PH	PH				
					WATER	WATER			NITROGEN	
			SPECIFIC		WHOLE	WHOLE	AMMONIA		AMMONIA +	
		TEMPER-	CON-	OXYGEN,	FIELD	LAB	DIS-	DIS-	ORGANIC	
LOCAL		ATURE	DUCT-	DIS-	(STAND-	(STAND-	SOLVED	SOLVED	DISSOLVED	
IDENTIFIER	DATE	WATER	ANCE	SOLVED	ARD	ARD	(MG/L	(MG/L	(MG/L	
		(DEG°C)	$(\mu S/CM)$	(MG/L)	UNITS)	UNITS)	AS N)	AS N)	AS N)	
Site 4 (Continued)										
A10	12-12-96	23.9	1636.	.7	6.74	6.92	.56	<.01	1.4	
A10	05-11-98	26.6	1757.	1.	6.62	7.01	.38	<.01	1.1	
A20	12-12-96	25.5	1286.	.6	7.1	7.1	1.	<.01	1.5	
A20	05-11-98	24.2	1174.	.7	7.01	7.38	.69	<.01	.98	
B20	12-11-96	24.5	817.	.9	6.85	7.46	.083	<.01	.45	
B20	05-12-98	24.	1058.		6.99	7.	.076	<.01	.4	
в5	12-11-96	22.5			6.87	7.54	<.01	.068	.48	
в5	05-13-98	22.7	1563.	.9	7.02					
B10	12-11-96	23.2	1121.	.9	6.96	7.5	.026	.058	.41	
B10	05-12-98	25.	1436.	.9	7.04	7.29	<.01	.028	.4	
51	12-12-96	17.67	1128.	7.28	6.74	8.04	.012	<.01	.87	
S1	05-13-98	27.3	728.	.9	6.87	7.28	.056	<.01	1.	
S2	12-12-96	19.99	970.	2.9	7.06	7.57	.054	<.01	.59	
S2	05-13-98	28.2	1359.	1.4	7.16	6.96	<.01	<.01	.62	
S2	05-13-98					5.68	<.01	<.01	<.2	
						· — — ·			· — — — ·	
Site 3										
A5	12-03-96	23.8	1020.		7.8	7.44	.03	<.01	.34	
A10	12-02-96	23.8	1382.	1.3	6.81	7.27	.071	<.01	.39	
A20	12-02-96	24.	2200.	1.	6.87	7.09	.17	<.01	.39	
A5F	12-03-96									
B20	12-03-96	24.3	2090.	.5	6.84	7.21	.1	<.01	.32	
В10	12-03-96	23.8	1340.	1.3	6.92	7.35	.017	<.01	.22	
B5F	12-03-96		1912.		6.77	7.12	.84	.012	1.4	
S1	12-04-96	20.48	2017.	2.96	7.37	7.74	<.01	<.01	.67	
S2	12-04-96	21.06	2005.	.1	7.68	7.86	.016	<.01	.74	
FLORIDAN	12-13-96		3520.		7.77	8.21	.51	<.01	.54	
Reference Site										
A5	11-22-96	23.8	98.8	.9	3.96	3.9	.052	.015	.84	
A5	07-09-97		387.	1.	3.64		.086	.018	1.4	
A5	05-07-98	24.9	129.6	.75	3.81	3.1	.052	<.01	.63	
A10	11-22-96		137.3	.35	5.01	5.06	.22	.016	1.1	
A10	07-09-97		115.	.55	5.17		.18	<.01	.72	
A10	05-07-98		132.	.7	5.42	5.69	. 31	<.01	.92	
A20	11-22-96		349.	.5	6.81	7.22	. 43	<.01	.64	
A20	07-08-97		459.	.6	6.72		. 48	<.01	.69	
A20	05-06-98		387.	.35	6.79	7.1	.54	<.01	.89	
A20	05-06-98					7.16	.55	<.01	.93	
B5						5.78	.064	<.01	.55	
-		23.6	88.7		5.8				·	
35	11-26-96		88.7 137.3	 1.5	5.8 5.91			<.01	.64	
	11-26-96 05-08-98	22.	137.3	1.5	5.91	5.65	.13	<.01 <.01	.64 <.2	
B10	11-26-96 05-08-98 11-26-96	22.	137.3	1.5	5.91	5.65 5.63	.13 <.01	<.01	<.2	
B10 B10	11-26-96 05-08-98 11-26-96 11-26-96	22. 24.7	137.3 306.	1.5 .55	5.91 5.41	5.65 5.63 5.53	.13 <.01 .22	<.01 .014	<.2 1.5	
B10 B10 B10	11-26-96 05-08-98 11-26-96 11-26-96 11-26-96	22. 24.7 24.7	137.3 306. 306.	1.5 .55 .55	5.91 5.41 5.41	5.65 5.63 5.53 5.62	.13 <.01 .22 .23	<.01 .014 .015	<.2 1.5 1.5	
B10 B10 B10 B10	11-26-96 05-08-98 11-26-96 11-26-96 11-26-96 05-08-98	22. 24.7 24.7 24.	137.3 306. 306. 219.	1.5 .55 .55 1.	5.91 5.41 5.41 5.32	5.65 5.63 5.53 5.62 5.62	.13 <.01 .22 .23 .21	<.01 .014 .015 .01	<.2 1.5 1.5 1.1	
B5 B10 B10 B10 B10 S1 S1	11-26-96 05-08-98 11-26-96 11-26-96 11-26-96 05-08-98 11-26-96	22. 24.7 24.7 24. 	137.3 306. 306. 219. 532.	1.5 .55 .55 1. 5.6	5.91 5.41 5.32 7.13	5.65 5.63 5.53 5.62 5.62 7.83	.13 <.01 .22 .23 .21 .042	<.01 .014 .015 .01 .01	<.2 1.5 1.1 .55	
B10 B10 B10 B10	11-26-96 05-08-98 11-26-96 11-26-96 11-26-96 05-08-98	22. 24.7 24.7 24. 	137.3 306. 306. 219.	1.5 .55 .55 1.	5.91 5.41 5.41 5.32	5.65 5.63 5.53 5.62 5.62	.13 <.01 .22 .23 .21	<.01 .014 .015 .01	<.2 1.5 1.5 1.1	

		NITRO-		PHOS-						
		GEN,	PHOS-	PHORUS	CARBON,		MAGNE-		POTAS-	
		NO2+NO3	PHORUS	ORTHO,	ORGANIC	CALCIUM	SIUM,	SODIUM,	SIUM,	
		DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	
IDENTIFIER	DATE	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	
		AS N)	AS P)	AS P)	AS C)	AS CA)	AS MG)	AS NA)	AS K)	
ite 4 (Continue	ed)									
10	12-12-96	<.02	.02	<.01	77.	230.	26.	66.	14.	
10	05-11-98	<.02	.05	<.01	11.	260.	27.	90.	15.	
120	12-12-96	<.02	<.02	<.01	58.	160.	16.	86.	1.3	
120	05-11-98	<.02	<.02	<.01	8.8	150.	15.	85.	2.1	
20	12-11-96	<.02	<.02	<.01	48.	100.	11.	51.	6.5	
20	05-12-98	<.02	.02	<.01	3.7	160.	15.	38.	7.4	
5	12-11-96	1.5	<.02	<.01	55.	200.	23.	42.	15.	
5	05-13-98									
10	12-11-96	1.4	<.02	<.01	47.	170.	18.	30.	15.	
10	05-12-98	.75	.12	.1	5.7	240.	23.	37.	16.	
1	12-12-96	<.02	<.02	.02	52.	100.	18.	100.	5.5	
1	05-13-98	.04	.25	.22	23.	51.	11.	69.	3.9	
2	12-12-96	.03	<.02	<.01	54.	130.	19.	77.	5.2	
2	05-13-98	<.02	.02	<.01	12.	110.	22.	130.	4.7	
	05-13-98	<.02	<.02	<.01	<.1	<.02	.002	<.1	<.1	
			·							
te 3	10.00.00				CP	1.50		50		
	12-03-96	.03	.04	.04	67.	160.	11.	58.	17.	
	12-02-96	<.02	<.02	.02	70. 70	160.	20.	85.	14.	
•	12-02-96	<.02	.04	.05	70. 	290.	33.	150.	2.	
	12-03-96 12-03-96		.06	<.01	66.	210.	14.	180.	1.4	
)	12-03-96	<.02 <.02	<.02	<.01 <.01	66.	140.	14.	100.	13.	
r F	12-03-96	<.02	.33	.1	95.	200.	49.	110.	14.	
	12-03-90	<.02	.33	. 21	54.	110.	40.	200.	11.	
	12-04-96	<.02	.23	.21	54.	110.	39.	210.	11.	
RIDAN	12-13-96	<.02	<.02	<.01	33.	74.	73.	400.	12.	
erence Site										
	11-22-96	<.02	.13	.15	60.	1.2	.6	7.4	.2	
	07-09-97	<.02	.05	.06						
	05-07-98	.07	.05	.05	37.	.9	1.2	11.	.2	
0	11-22-96	<.02	.02	.04	64.	5.5	2.	15.	.8	
0	07-09-97	<.02	<.02	.04						
0	05-07-98	<.02	<.02	.02	28.	8.2	2.4	11.	.9	
0	11-22-96	<.02	.21	.15	52.	47.	3.	21.	.7	
0	07-08-97	<.02	.23	.16						
0	05-06-98	<.02	.17	.19	13.	54.	4.1	18.	.8	
)	05-06-98	<.02	.19	.22	14.	54.	4.1	17.	.8	
	11-26-96	.1	<.02	<.01	40.	4.4	.8	8.2	1.	
2	05-08-98	<.02	<.02	.02	18.	8.	1.1	13.	.8	
0	11-26-96	<.02	<.02	<.01	2.5	<.01	<.002		<.1	
0	11-26-96	<.02	<.02	<.01	79.	21.	5.	26.	.9	
0	11-26-96	<.02	<.02	<.01	77.	22.	5.	28.	.9	
0	05-08-98	<.02 .04	<.02	.01	53. 73.	15. 71	3.3	20. 29.	.8	
	11-26-96 11-26-96	.04	<.02 <.02	.01 .01	73.	71. 71.	5. 5.	29. 29.	. 4 . 4	
			<.UZ	. U T	13.	/	J.	47.	. 1	
	11-26-96	.04	<.02	.01	73.	71.	5.	29.	. 4	

. .			-						
		CHLO-		FLUO-	SILICA,	100		BERYL-	A
		RIDE,	SULFATE	RIDE,	DIS-	ARSENIC		LIUM,	CADMIUM
LOCAL		DIS-	DIS-	DIS-	SOLVED	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	(MG/L	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(MG/L	(MG/L	(MG/L	AS	(µG/L	(µG/L	(µG/L	(µG/L
		AS CL)	AS SO4)	AS F)	SIO2)	AS AS)	AS BA)	AS BE)	AS CD)
Site 4 (Continue	ed)								
A10	12-12-96	160.	320.	.2	18.	5.5	120.	<.5	1.4
A10	05-11-98	160.	430.	.28	13.				
A20	12-12-96	97.	290.	.5	16.	<1.	74.	<.5	1.1
A20	05-11-98	75.	260.	.44	15.				
B20	12-11-96	35.	150.	.7	15.	3.	46.	<.5	<.5
В20	05-12-98	49.	270.	.61	14.				
В5	12-11-96	100.	340.	.5	7.7	1.5	120.	<.5	<.5
В5	05-13-98								
B10	12-11-96	74.	260.	.5	6.6	1.6	96.	<.5	<.5
в10	05-12-98	82.	430.	.57	7.3				
S1	12-12-96	220.	110.	.4	5.4	<1.	39.	<.5	<.5
S1	05-13-98	140.	41.	.22	5.3				
S2	12-12-96	120.	200.	.6	15.	<1.	45.	<.5	<.5
S2	05-13-98	240.	140.	.43	12.				
S2	05-13-98	<.1	<.2	<.1	<.01				
Site 3									
A5	12-03-96	130.	97.	.8	14.	2.1	94.	<.5	<.5
A10	12-02-96	190.	140.	.6	14.	<1.	89.	<.5	<.5
A20	12-02-96	430.	310.	. 4	17.	<1.	44.	<.5	<.5
A5F	12-03-96					1.8	120.	<.5	<.5
B20	12-03-96	420.	150.	.4	15.	<1.	39.	<.5	.7
B10	12-03-96	200.	85.	. 8	10.	<1.	130.	<.5	<.5
B5F	12-03-96	370.	77.	1.1	14.	16.	130.	<.5	<.5
S1	12-04-96	450.	120.	.5	10.	<1.	43.	<.5	<.5
S2	12-04-96	450.	120.	.5	10.	<1.	44.	<.5	<.5
FLORIDAN	12-13-96	960.	130.	.5	13.	<1.	27.	<.5	<.5
								· — — ·	
Reference Site					• -	<u>.</u>		_	_
A5	11-22-96	14.	1.8	<.1	8.7	1.4	16.	<.5	<.5
A5	07-09-97								
A5	05-07-98	19.	5.9	<.1	8.1				
A10	11-22-96	26.	4.3	<.1	8.2	4.1	19.	<.5	<.5
A10 A10	07-09-97 05-07-98	21.			10.				
A10 A20	05-07-98 11-22-96	21. 16.	4.3	<.1 .2	10.	9.8	23.	<.5	 <.5
A20 A20	07-08-97	16.	.9	. 2		9.8	23.	<.5	<.5
A20 A20	07-08-97	20.	.2	.17					
A20 A20	05-06-98	20.	.2	.17	11. 11.				
B5	11-26-96	13.	.2 6.7	.1/ <.1	11. 7.4	3.4	6.	<.5	<.5
B5	05-08-98	26.	8.1	<.1	7.4			<.5	
B10	11-26-96	<.1	<.2	<.1	.1	<1.	<.2	<.5	<.5
B10	11-26-96	61.	6.6	<.1	18.	1.	37.	<.5	<.5
B10	11-26-96	61.	6.5	<.1	19.	1.4	38.	<.5	<.5
B10	05-08-98	41.	4.9	<.1	15.				
s1	11-26-96	54.	6.	.2	10.	<1.	13.	<.5	<.5
S1	11-26-96	54.	6.	.2	10.	<1.	13.	<.5	<.5
S1	11-26-96	54.	6.	.2	10.	<1.	13.	<.5	<.5
S1	07-09-97								

		CHRO-					MANGA-	MOLYB-	
		MIUM,	COBALT,	COPPER,	IRON,	LEAD,	NESE,	DENUM,	NICKEL,
		DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(µG/L	(µG/L	$(\mu G/L$	(µG/L	$(\mu G/L$	$(\mu G/L$	(µG/L	$(\mu G/L$
		AS CR)	AS CO)	AS CU)	AS FE)	AS PB)	AS MN)	AS MO)	AS NI)
ite 4 (Continue	ed)								
0	12-12-96	<1.	1.4	<1.	19000.	1.3	240.	13.	5.5
LO	05-11-98				15527.		130.		
20	12-12-96	<1.	<1.	<1.	15000.	<1.	100.	31.	5.
0	05-11-98				11077.		100.		
20	12-11-96	<1.	<1.	<1.	5100.	<1.	84.	51.	2.8
0	05-12-98				15094.		140.		
	12-11-96	<1.	<1.	2.1	5.	<1.	29.	31.	3.9
	05-13-98								
0	12-11-96	<1.	<1.	<1.	90.	<1.	67.	38.	2.8
0	05-12-98				6.		27.		
0	12-12-96	<1.	<1.	2.6	60.	<1.	6.9	3.9	1.3
	05-13-98				540.		36.		
	12-12-96	<1.	<1.	<1.	40.	<1.	56.	25.	1.4
	05-13-98				40.		10.		
	05-13-98				2.		<.2		
e 3									
	12-03-96	<1.	<1.	1.3	3.	<1.	66.	27.	2.1
	12-02-96	<1.	<1.	<1.	830.	<1.	51.	15.	1.5
	12-02-96	<1.	<1.	<1.	1500.	<1.	100.	2.2	<1.
	12-03-96	<1.	<1.	<1.		<1.		13.	8.
	12-03-96	<1.	<1.	<1.	7300.	<1.	49.	17.	<1.
I.	12-03-96	<1.	<1.	<1.	400.	<1.	10.	21.	1.6
,	12-03-96	<1.	2.	<1.	2500.	<1.	490.	25.	5.2
	12-04-96	<1.	<1.	2.7	30.	<1.	34.	2.7	1.3
	12-04-96	<1.	<1.	2.3	30.	<1.	43.	3.1	1.
ORIDAN	12-13-96	<1.	<1.	<1.	20.	<1.	14.	<2.	<1.
erence Site	11 00 00	2 0	-1	2 0	25.0.0	10	0.0	- 2	1 🗖
	11-22-96	2.9	<1.	3.9	2500.	13.	8.2	<2.	1.7
	07-09-97								
2	05-07-98				2100.		3.7		
0	11-22-96	4.3	<1.	10.	2400.	4.4	7.7	<2.	1.3
0	07-09-97								
.0	05-07-98				3200.		8.3	 E 2	
0	11-22-96	<1.	<1.	<1.	3700.	<1.	7.1	5.3	<1.
0	07-08-97								
0	05-06-98				5500.		9.2		
0	05-06-98				5600.		9.		
	11-26-96	1.6	<1.	1.5	1800.	<1.	19.	<2.	1.2
.	05-08-98				5300.		56.		
0	11-26-96	<1.	<1.	<1.	<1.	<1.	<.2	<2.	<1.
0	11-26-96	3.3	<1.	<1.	4600.	<1.	11.	<2.	<1.
0	11-26-96	3.3	<1.	<1.	4800.	<1.	12.	<2.	<1.
)	05-08-98				3400.		7.7		
	11-26-96	<1.	<1.	<1.	190.	<1.	4.5	<2.	<1.
	11-26-96	<1.	<1.	<1.	190.	<1.	4.5	<2.	<1.
	11-26-96	<1.	<1.	<1.	190.	<1.	4.5	<2.	<1.
	07-09-97								

						ALKA-	SOLIDS,		C-13/
				ALUM-	SELE-	LINITY	RESIDUE		C-12
		SILVER,	ZINC,	INUM,	NIUM,	WAT DIS	AT 180	BROMIDE	STABLE
		DIS-	DIS-	DIS-	DIS-	TOT IT	DEG. C	DIS-	ISOTOPE
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	FIELD	DIS-	SOLVED	RATIO
IDENTIFIER	DATE	$(\mu G/L$	$(\mu G/L$	$(\mu G/L$	$(\mu G/L$	MG/L AS	SOLVED	(MG/L	PER
		AS AG)	AS ZN)	AS AL)	AS SE)	CACO3	(MG/L)	AS BR)	MIL
Site 4 (Continue	d)								
A10	12-12-96	<1.	10.	41.	<1.	332.	1110.	.49	
A10	05-11-98						1260.	.4	-13.83
A20	12-12-96	<1.	4.3	35.	<1.	270.	848.	.37	-13.05
A20	05-11-98		4.5		<ı. 	270.	800.	.3/	-10.91
B20	12-11-96	<1.	1.2	16.	<1.	228.	528.	. 3	-10.91
					<ı. 			.14	
B20	05-12-98						783.		-8.53
B5	12-11-96	<1.	1.9	<3.	1.2	254.	956.	.28	
B5	05-13-98								-12.91
B10	12-11-96	<1.	1.4	<3.	1.3	228.	790.	. 23	
B10	05-12-98						1060.	. 2	-11.04
S1	12-12-96	<1.	8.9	<3.	<1.	176.	792.	.71	
S1	05-13-98						462.	. 8	-11.02
S2	12-12-96	<1.	3.6	4.9	<1.	208.	740.	. 4	
S2	05-13-98						814.	.9	-7.54
S2	05-13-98						4.	<.05	
Site 3	10.00.00	.1	15	2 6	-1	240	720	4.0	
A5	12-03-96	<1.	15.	3.6	<1.	340.	732.	. 48	
A10	12-02-96	<1.	2.5	5.	1.1	296.	856.	.65	
A20	12-02-96	<1.	1.4	6.9	<1.	306.	1670.	1.4	
A5F	12-03-96	<1.	12.	<3.	<1.				
B20	12-03-96	<1.	2.5	21.	<1.	302.	1420.	1.4	
B10	12-03-96	<1.	1.5	<3.	<1.	304.	806.	.67	
B5F	12-03-96	<1.	9.9	3.9	1.4	410.	1340.	1.	
S1	12-04-96	<1.	14.	<3.	1.6	190.	1190.	1.5	
S2	12-04-96	<1.	14.	4.7	1.4	186.	1190.	1.6	
FLORIDAN	12-13-96	<1.	1.5	<3.	<1.	107.	2060.	3.4	
Reference Site									
A5	11-22-96	<1.	13.	1100.	1.		126.	<.1	
A5	07-09-97								
A5	05-07-98						106.	<.05	
A10	11-22-96	<1.	4.	1700.	1.4	9.2	156.	<.1	
A10	07-09-97					26.			
A10	05-07-98						128.	.1	
A20	11-22-96	<1.	<1.	16.	<1.	196.	214.	<.1	
A20	07-08-97					186.			
A20	05-06-98						240.	.1	
A20	05-06-98						236.	.1	
B5	11-26-96	<1.	3.1	540.	1.2		80.	<.1	
B5	05-08-98						122.	<.05	-20.38
B10	11-26-96	<1.	<1.	<3.	<1.		<1.	<.1	-20.30
B10	11-26-96	<1.	6.1	1100.	1.2	38.	350.	.15	
B10 B10	11-26-96	<1.	2.4	1100.	1.1	38.	354.	.15	
B10	05-08-98		2.4				248.	.14	-22.09
S1	11-26-96	<1.	2.4	4.3	1.	188.	240. 366.	.2	-22.09
					1.				
S1	11-26-96	<1.	2.4	4.3		188.	366.	.15	
S1	11-26-96	<1.	2.4	4.3	1.	188.	366.	.15	
S1	07-09-97					184.			

		H-2/	0-18/			N15/N14	N15/N14	SDF-	ANC
		H-2/ H-1	0-16			NO3	NH4	CIFIC	UNFLTRD
		STABLE	STABLE	N15/N14	N15/N14		FRAC	CON-	TIT 4.5
		ISOTOPE	ISOTOPE	NO3	NH4	WATER	WATER	DUCT-	LAB
LOCAL		RATIO	RATIO	FRAC	FRAC	FLTRD	FLTRD	ANCE	(MG/L
IDENTIFIER	DATE	PER	PER	SOIL	SOIL	0.45 U	0.45 U	LAB	AS
		MIL	MIL			PER MIL			CACO3)
Site 4 (Continu	od)								
10 4 (Concinu	12-12-96	-15.6	-2.94					1570.	288.
110	05-11-98	-11.3	-2.65				6.2	1720.	281.
120	12-12-96	-8.7	-2.34					1250.	237.
120	05-11-98		-2.52				5.2	1140.	236.
320	12-11-96	-11.	-2.89					804.	215.
320	05-12-98	-23.2	-4.15					1020.	196.
35	12-11-96	-22.8	-4.36					1360.	236.
35	05-13-98	-13.5	-2.83			28.3			
310	12-11-96	-22.7	-4.27					1110.	216.
310	05-12-98	-16.8	-3.45			27.1		1430.	246.
31	12-12-96	9	-1.09					1220.	172.
31	05-13-98	.9	48					723.	92.
2	12-12-96	-11.4	-2.33					1140.	201.
32	05-13-98	-2.6	-1.14					1380.	187.
32	05-13-98							1200.	4.4
		· — — ·			· — — ·				
Site 3									
15	12-03-96		-3.38					1180.	314.
10	12-02-96		-3.19					1400.	305.
20	12-02-96	-8.5	-2.3					2380.	304.
15F	12-03-96								
320	12-03-96	-9.4	-2.21					2110.	291.
310	12-03-96	-14.6	-2.94					1350.	294.
35F	12-03-96	-8.1	-2.14					2020.	416.
31	12-04-96		-1.14					2000.	185.
32	12-04-96		-1.1					2040.	185.
LORIDAN	12-13-96	-2.8	-1.43					3530.	102.
eference Site									
.5	11-22-96	-10.1	-2.7					104.	<1.
15	07-09-97								
45	05-07-98	-14.9	-3.11					136.	<1.
10	11-22-96	-15.4	-3.34					144.	5.3
10	07-09-97						4.3		
10	05-07-98	-14.	-3.01				4.1	115.	12.
120	11-22-96	-11.1	-2.77					411.	168.
120	07-08-97								
.20	05-06-98	-13.	-2.96				б.	375.	164.
.20	05-06-98							368.	160.
5	11-26-96	-7.9	-2.3					84.	7.1
35	05-08-98	-17.9	-3.77				4.4	130.	6.2
310	11-26-96							<1.	4.2
310	11-26-96	-17.9	-3.99					295.	23.
310	11-26-96							291.	23.
310	05-08-98	-14.4	-3.34				2.6	212.	22.
31	11-26-96	-10.4	-2.38					535.	187.
31	11-26-96	-10.4	-2.38					535.	187.
31 31	11-26-96 07-09-97	-10.4	-2.38					535.	187.

					PH	PH			
					WATER	WATER	NTTDOCEN	NTTROCEN	NITROGEN
			SPECIFIC		WHOLE	WHOLE		NITRITE	AMMONIA +
		MEMDED		OWNERD					
LOGAL		TEMPER-	CON-	OXYGEN,	FIELD	LAB	DIS-	DIS-	ORGANIC
LOCAL	DAUE	ATURE	DUCT-	DIS-	(STAND-	(STAND-	SOLVED	SOLVED	DISSOLVED
IDENTIFIER	DATE	WATER	ANCE	SOLVED	ARD	ARD	(MG/L	(MG/L	(MG/L
		(DEG°C)	(µS/CM)	(MG/L)	UNITS)	UNITS)	AS N)	AS N)	AS N)
Reference Site (Continued)									
S1	07-09-97	27.	522.	.3	7.2		.02	<.01	.5
S1	07-09-97	27.	522.	.3	7.2		.02	<.01	.5
S1	05-08-98	28.	258.	5.55	7.08	7.49	.013	<.01	.57
S1	05-08-98	28.	258.	5.55	7.08	7.49	.013	<.01	.57
S1	05-08-98	28.	258.	5.55	7.08	7.49	.013	<.01	.57
RAINFALL	11-26-96								
RAINFALL	06-08-98						S.265	.033	.371
Site 2									
FERTILIZER	07-10-98								
A5	12-10-96	20.5	793.		7.3	7.31	2.5	.013	3.3
А5	07-10-97	26.8	1195.	2.	4.08		6.2	<.01	7.8
A5	05-18-98	24.	310.	3.7	6.8	6.85	.02	<.01	.69
A10	12-10-96	22.4	1257.	1.	6.1	7.7	.014	.38	.7
A10	07-10-97	25.2	1268.	.7	7.21		.026	.11	.83
A10	05-18-98	25.1	1124.	.85	7.14	7.54	<.01	.032	.75
A20	12-10-96	23.4	1753.	.7	6.7	7.26	.33	<.01	1.3
A20	12-10-96	23.4	1753.	.7	6.7	7.16	.33	<.01	1.3
A20	07-10-97	24.1	1624.	.6	7.07		.28	<.01	1.4
A20	05-18-98	24.	1559.	.5	7.03	7.15	.36	<.01	1.3
A5F	12-10-96	20.5	893.		6.93	7.59	.47	<.01	1.6
A5F	07-10-97	27.		2.2			1.4	<.01	4.
A5F	05-18-98	23.2	619.	1.5	6.63	7.02	.35	<.01	1.4
B20	12-09-96	23.2	1551.	.85	7.24	7.33	.54	<.01	1.3
B20	07-28-97						.57	<.01	1.6
B20	05-19-98	23.9	1629.	.5	7.1	7.43	.64	<.01	1.2
в5	12-09-96	20.8	1231.		7.24	6.91	.59	.022	1.4
в5	07-28-97						.81	.024	3.6
в5	05-19-98	23.5	456.	1.6	5.11	4.55	.09	.02	1.1
B10	12-09-96	21.4	1153.		7.36	7.42	.97	<.01	1.6
B10	07-28-97								
B10	05-19-98	24.7	902.	2.4	7.24	7.57	.17	.12	.72
B5F	12-09-96	24.1	1094.		7.35	7.68	.76	<.01	1.6
B5F	05-19-98	23.5	827.	.1	7.49	7.56	.6	<.01	1.5
S1	12-09-96	16.83	1100.	4.53	7.32	7.89	.076	<.01	.84
Sl	12-09-96	16.83	1100.	4.53	7.32	7.84	.078	<.01	.9
S1	07-10-97	29.25	980.	1.8	7.14		.064	.014	.86
S1	05-19-98	27.	1199.	.1	7.58	8.16	<.01	<.01	.83
Site 1									
A10	12-06-96	26.6	1664.		5.9	5.98	1.5	.019	2.
A20	12-06-96	23.4	1696.	.6	6.86	7.12	.19	<.01	.54
B20	12-05-96	23.2	1707.	.7	6.7	7.1	.24	<.01	.62
В5	12-05-96		2740.		5.61	6.11	2.4	.053	3.3
B10	12-05-96	24.	2390.		4.68	5.02	4.4	.034	4.5
S1	12-06-96	23.74	2150.	.85	7.04	7.69	.4	.02	.58

		NTEDO		DUOG					
		NITRO- GEN,	PHOS-	PHOS- PHORUS	CARBON,		MAGNE-		POTAS-
		NO2+NO3	PHOS-	ORTHO,		CALCIUM	SIUM,	SODIUM,	SIUM,
		DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L	(MG/L
		AS N)	AS P)	AS P)	AS C)	AS CA)	AS MG)	AS NA)	AS K)
rence Site	(Continued)								
	07-09-97	<.02	<.02	<.01					
	07-09-97	<.02	<.02	<.01					
	05-08-98	.13	<.02	<.01	21.	28.	3.6	15.	1.
	05-08-98	.13	<.02	<.01	21.	28.	3.6	15.	1.
	05-08-98	.13	<.02	<.01	21.	28.	3.6	15.	1.
NFALL	11-26-96								
FALL	06-08-98	.212	.01	.022					
· — — —			· — — ·						
2									
ILIZER	07-10-98								
	12-10-96	4.	.03	.03	25.	76.	16.	29.	26.
	07-10-97		.07 <.02	.08 <.01	 8.7	45.	10.		 13.
	05-18-98	.51 .83	<.02 <.02	<.01 .01	33.	45. 120.	24.	16. 70.	13.
	12-10-96 07-10-97	4.9	<.02	.01					
	05-18-98	.87	<.02	.02	9.3	130.	21.	51.	14.
	12-10-96	<.02	<.02	<.01	55.	250.	21.	82.	.7
	12-10-96	<.02	<.02	<.01	55.	250.	21.	83.	.6
	07-10-97	<.02	<.02	.01					
	05-18-98	<.02	<.02	<.01	18.	220.	18.	80.	.6
	12-10-96	<.02	<.02	<.01	50.	120.	18.	37.	7.9
	07-10-97	<.02	<.02	.02					
	05-18-98	<.02	<.02	.02	17.	60.	10.	31.	5.7
	12-09-96	<.02	<.02	<.01	55.	220.	24.	61.	1.2
	07-28-97	<.02	.36	<.01					
	05-19-98	<.02	<.02	<.01	15.	240.	26.	61.	1.
	12-09-96	2.4	<.02	<.01	16.	110.	23.	71.	18.
	07-28-97	20.	.11	.01					
	05-19-98	8.3	<.02	.01	11.	42.	14.	6.9	9.4
	12-09-96	.02	<.02	<.01	43.	140.	16.	57.	6.7
	07-28-97								
	05-19-98	.97	<.02	.01	8.4	120.	15.	37.	10.
	12-09-96	.07	.06	.06	45.	100.	15.	76.	11.
	05-19-98	<.02	.03	.05	12.	81.	13.	42.	11.
	12-09-96	.03	.04	.03	55.	130.	20.	88.	8.
	12-09-96	.03	.04	.03		120.	20.	90.	7.6
	07-10-97	.06	.12	.14					
	05-19-98	<.02	.03	.03	14.	120.	18.	79.	5.5
e 1	12.06.06	20	< 02	< 01	1.2	0 /	57	100	2 F
	12-06-96		<.02	<.01	12.	84.	57.	120.	25.
	12-06-96	<.02	<.02	<.01	48.	260.	б.	78.	.9
	12-05-96	<.02	<.02	<.01	79. 20	280.	8.	67.	.9
	12-05-96 12-05-96	14. .04	<.02 <.02	<.01 <.01	30.	150. 170.	100. 46.	190. 160.	69. 14.
	12-05-96	.04	<.02 <.02	.01		170. 91.	40. 60.	260.	14. 8.2
	12-06-96	.08	<.02 <.02	.01		91. 91.	60.	260.	8.2
	12-00-90	.00	<.UZ	.01		21.	00.	200.	0.4

		CHLO-		FLUO-	SILICA,			BERYL-	
		RIDE,	SULFATE	RIDE,	DIS-	ARSENIC	BARIUM,	LIUM,	CADMIUM
		DIS-	DIS-	DIS-	SOLVED	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	(MG/L	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(MG/L	(MG/L	(MG/L	AS	$(\mu G/L$	$(\mu G/L$	(µG/L	$(\mu G/L$
		AS CL)	AS SO4)	AS F)	SIO2)	AS AS)	AS BA)	AS BE)	AS CD)
eference Site ((Continued)								
31	07-09-97								
1	07-09-97								
1	05-08-98	24.	13.	.18	8.2				
1	05-08-98	24.	13.	.18	8.2				
1	05-08-98	24.	13.	.18	8.2				
AINFALL	11-26-96								
AINFALL	06-08-98								
ite 2									
ERTILIZER	07-10-98								
.5	12-10-96	46.	220.	.5	13.	1.4	99.	<.5	<.5
5	07-10-97								
5	05-18-98	45.	81.	.33	15.				
10	12-10-96	170.	240.	.6	9.2	1.2	82.	<.5	<.5
10	07-10-97								
10	05-18-98	140.	250.	.5	12.				
20	12-10-96	250.	370.	.2	10.	1.2	110.	<.5	.7
0	12-10-96	250.	370.	.2	10.	1.3	120.	<.5	.7
0	07-10-97								
0	05-18-98	200.	320.	.19	11.				
7	12-10-96	70.	190.	.3	16.	1.5	100.	<.5	<.5
	07-10-97								
F	05-18-98	39.	130.	.42	12.				
C	12-09-96	210.	320.	.3	12.	<1.	110.	<.5	<.5
0	07-28-97								
0	05-19-98	210.	380.	.25	11.				
	12-09-96	160.	290.	.6	12.	1.1	75.	<.5	.7
	07-28-97								
i	05-19-98	19.	140.	.56	20.				
10	12-09-96	100.	280.	.2	9.	2.8	110.	<.5	.5
.0	07-28-97								
.0	05-19-98	79.	200.	.42	9.4				
F	12-09-96	120.	180.	.4	11.	2.1	68.	<.5	<.5
5F	05-19-98	39.	120.	.44	13.				
L	12-09-96	180.	160.	.4	9.1	1.5	63.	<.5	<.5
	12-09-96	180.	160.	.4	9.1	1.6	64.	<.5	<.5
L	07-10-97								
	05-19-98	170.	160.	.41	10.				
.te 1 .0	12-06-96	240	300.	.1	7 2	1 0	72.	~ F	1.3
20	12-06-96	340. 310.	200.	.1	7.3 17.	1.2 1.6	53.	<.5 <.5	1.3 <.5
									<.5 .6
10	12-05-96	290. 540	210. 520	.3	18.	1.3	54. 75	<.5	
0	12-05-96	540. 540	530. 460	<.1	40. 26	<1.	75.	<.5	<.5
.0	12-05-96	540. 580	460. 150	<.1	26. 17	<1.	74. 57	.7	7.
	12-06-96	580. 580	150. 150	.6	17.	1.	57.	<.5	<.5
L	12-06-96	580.	150.	.6	17.	1.	57.	<.5	<.5

		CHRO-					MANGA-	MOLYB-	
		MIUM,	COBALT,	COPPER,	IRON,	LEAD,	NESE,	DENUM,	NICKEL,
		DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-	DIS-
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED	SOLVED
IDENTIFIER	DATE	(μG/L	(μG/L	(μG/L	(µG/L	(μG/L	(µG/L	(μG/L	(µG/L
		AS CR)	AS CO)	AS CU)	AS FE)	AS PB)	AS MN)	AS MO)	AS NI)
erence Site	(Continued)								
	07-09-97								
	07-09-97								
	05-08-98				110.		2.6		
	05-08-98				110.		2.6		
	05-08-98				110.		2.6		
NFALL	11-26-96								
NFALL	06-08-98								
2	A- - - - - -								
TILIZER	07-10-98								
	12-10-96	<1.	1.1	12.	50.	<1.	540.	<2.	4.6
	07-10-97								
	05-18-98				30.		280.		
	12-10-96	<1.	<1.	2.4	20.	<1.	270.	5.	4.4
	07-10-97								
	05-18-98				30.		340.		
	12-10-96	<1.	<1.	<1.	8700.	<1.	58.	5.1	<1.
	12-10-96	<1.	<1.	<1.	8300.	<1.	59.	5.6	<1.
	07-10-97								
	05-18-98				6600.		42.		
	12-10-96	<1.	<1.	<1.	4300.	<1.	160.	<2.	1.8
	07-10-97								
	05-18-98				6700.		170.		
	12-09-96	<1.	<1.	<1.	2600.	<1.	30.	5.1	<1.
	07-28-97								
	05-19-98				2900.		16.		
	12-09-96	<1.	3.1	8.4	1400.	<1.	430.	<2.	9.8
	07-28-97								
	05-19-98				600.		500.		
	12-09-96	<1.	<1.	<1.	6800.	<1.	240.	7.8	2.6
	07-28-97								
	05-19-98				270.		220.		
	12-09-96 05-19-98	<1.	<1.	<1.	1400. 2700.	<1.	290.	9.2	1.5
		<1.					290. 18.		<1.
	12-09-96				40. 40.	<1. <1.		3.6 4.	
	12-09-96	<1.	<1.	3.6	40.	<1.	18.	4.	<1.
	07-10-97				30.		8.2		
	05-19-98				30.		8.∠		
e 1									
	12-06-96	<1.	4.8	<1.	13000.	<1.	91.	<2.	4.7
	12-06-96	<1.	<1.	<1.	2600.	<1.	37.	<2.	<1.
	12-05-96	<1.	<1.	<1.	7500.	<1.	36.	<2.	<1.
	12-05-96	<1.	1.1		150.	<1.	480.	<2.	1.3
	12-05-96	<1.	8.6	<1.	89000.	4.3	220.	<2.	11.
	12-06-96	<1.	<1.	<1.	20.	<1.5	3.	<2.	<1.
	12-06-96	<1.	<1.	<1.	20.	<1.	3.	<2.	<1.
	00 00				20.		5.		

									a 10 (
					0.01 -	ALKA-	SOLIDS,		C-13/
				ALUM-	SELE-	LINITY	RESIDUE	DD00000	C-12
		SILVER,	ZINC,	INUM,	NIUM,	WAT DIS	AT 180	BROMIDE	STABLE
LOGIL		DIS-	DIS-	DIS-	DIS-	TOT IT	DEG. C	DIS-	ISOTOPE
LOCAL		SOLVED	SOLVED	SOLVED	SOLVED	FIELD	DIS-	SOLVED	RATIO
IDENTIFIER	DATE	(µG/L	(µG/L	(µG/L	(µG/L	MG/L AS	SOLVED	(MG/L	PER
		AS AG)	AS ZN)	AS AL)	AS SE)	CACO3	(MG/L)	AS BR)	MIL
Reference Site	(Continued)								
S1	07-09-97					184.			
S1	07-09-97					184.			
S1	05-08-98						186.	.09	-13.65
31	05-08-98						186.	.09	-13.65
51	05-08-98						186.	.09	-13.65
RAINFALL	11-26-96								
RAINFALL	06-08-98								
·									
Site 2									
FERTILIZER	07-10-98								
15	12-10-96	<1.	150.	61.	1.4		542.	.17	
.5	07-10-97								
15	05-18-98						298.	.1	
10	12-10-96	<1.	4.8	6.9	1.8		774.	.52	
110	07-10-97					141.			
10	05-18-98						788.	.4	-12.82
20	12-10-96	<1.	1.4	23.	1.3		1370.	.71	
20	12-10-96	<1.	3.2	17.	1.2		1420.	.72	
20	07-10-97					190.			
20	05-18-98						1150.	.8	-9.72
5F	12-10-96	<1.	2.2	26.	<1.		630.	.46	
5F	07-10-97								
F	05-18-98						410.	.3	
0	12-09-96	<1.	<1.	6.4	1.6		1210.	.63	
10	07-28-97								
0	05-19-98						1220.	.6	-11.67
	12-09-96	<1.	53.	140.	1.6		754.	.42	
	07-28-97								
5	05-19-98						332.	.09	
LO	12-09-96	<1.	11.	21.	1.3		744.	.42	
LO	07-28-97								
LO	05-19-98						598.	. 2	-11.43
5F	12-09-96	<1.	4.6	8.8	1.4		690.	. 46	-11.45
5F 5F	05-19-98						498.	.3	-12.21
1	12-09-96	<1.	12.	6.6	1.5		498. 804.	.53	-12.21
1	12-09-96	<1.	12. 9.5	7.7	1.2		776.	.53	
1	07-10-97					173.			
1	07-10-97						806.	.5	
ite 1									
10	12-06-96	<1.	30.	150.	1.6	18.	1020.	.83	
20	12-06-96	<1.	<1.	5.1	<1.0	228.	1480.	.93	
20	12-05-96	<1.	1.6	21.	1.3	248.	1360.	.86	
5	12-05-96	<1.	40.	690.	1.3	248.	1980.	1.3	
10	12-05-96	<1.	40. 61.	720.	1.5		1520.	1.5	
1	12-05-96	<1.	1.9	6.8	<1.	138.	1340.	2.	
1	12-06-96	<1.	1.9	6.8	<1.	138.	1340.	2.	
-	12 00-90	~+.	1.9	0.0	~±.	±00.	1010.	4.	

		0 (a 10/							
		H-2/	0-18/				N15/N14		ANC	
		H-1	0-16			NO3	NH4	CIFIC	UNFLTRD	
		STABLE	STABLE		N15/N14	FRAC	FRAC	CON-	TIT 4.5	
		ISOTOPE	ISOTOPE	NO3	NH4	WATER	WATER	DUCT-	LAB	
LOCAL	2200	RATIO	RATIO	FRAC	FRAC	FLTRD	FLTRD	ANCE	(MG/L	
IDENTIFIER	DATE	PER MIL	PER MIL	SOIL	SOIL PER MIL	0.45 U	0.45 U PER MIL	LAB	AS CACO3)	
		MIL	MIL	PER MIL	PER MIL	PER MIL	PER MIL	(µs/cm)	CACOS	
Reference Site	(Continued)									
31	07-09-97									
31	07-09-97									
31	05-08-98	-3.9	-1.01			1.9		262.	79.	
51	05-08-98	-3.9	-1.01			1.9		262.	79.	
31	05-08-98	-3.9	-1.01			1.9		262.	79.	
RAINFALL	11-26-96	-14.	-3.97							
RAINFALL	06-08-98	-18.	-3.9							
		· — — ·								
ite 2					_					
TERTILIZER	07-10-98			4.5	7					
45	12-10-96	-21.7	-4.46					797.	47.	
45	07-10-97					1.3	14.5			
45	05-18-98	-11.4	-2.38					331.	34.	
10	12-10-96	-6.3	-1.73					1200.	101.	
410	07-10-97									
10	05-18-98	-7.5	-1.87			26.3		1130.	105.	
20	12-10-96	-4.1	-1.52					1750.	175.	
120	12-10-96							1760.	174.	
20	07-10-97									
120	05-18-98	-5.	-1.52				6.1	1540.	191.	
15F	12-10-96	-11.3	-2.76					885.	161.	
15F	07-10-97						5.6			
15F	05-18-98	-10.3	-2.39				7.	611.	120.	
320	12-09-96	-6.1	-1.44					1560.	195.	
320	07-28-97									
320	05-19-98	-7.	-1.76				9.1	1600.	164.	
35	12-09-96	-8.6	-2.21					1140.	33.	
35	07-28-97									
35	05-19-98	-11.7	-2.88					455.	1.2	
310 310	12-09-96	-12.2	-2.76					1090.	157.	
310	07-28-97 05-19-98	-9.6				24.6	9.4	919.	153.	
310 85F	12-09-96		-2.38 -2.55			24.0	9.4	919. 1030.	153.	
35F	05-19-98		-2.55				10.4	818.	342.	
35F 31	12-09-96		-2.63						203.	
31	12-09-96	-1.8	92					1240.	203.	
51	07-10-97									
51	05-19-98	.4	46					1180.	199.	
ite 1										
10	12-06-96	-10.3	-2.69					1700.	13.	
.20	12-06-96	-9.2	-2.65					1700.	214.	
20	12-05-96	-10.4	-2.63					1710.	242.	
35	12-05-96	-11.3	-2.62					2800.	25.	
310	12-05-96	-5.8	-2.08					2410.	4.3	
31	12-06-96	-3.6	-1.61					2370.	133.	
s1	12-06-96	-3.6	-1.61					2370.	133.	