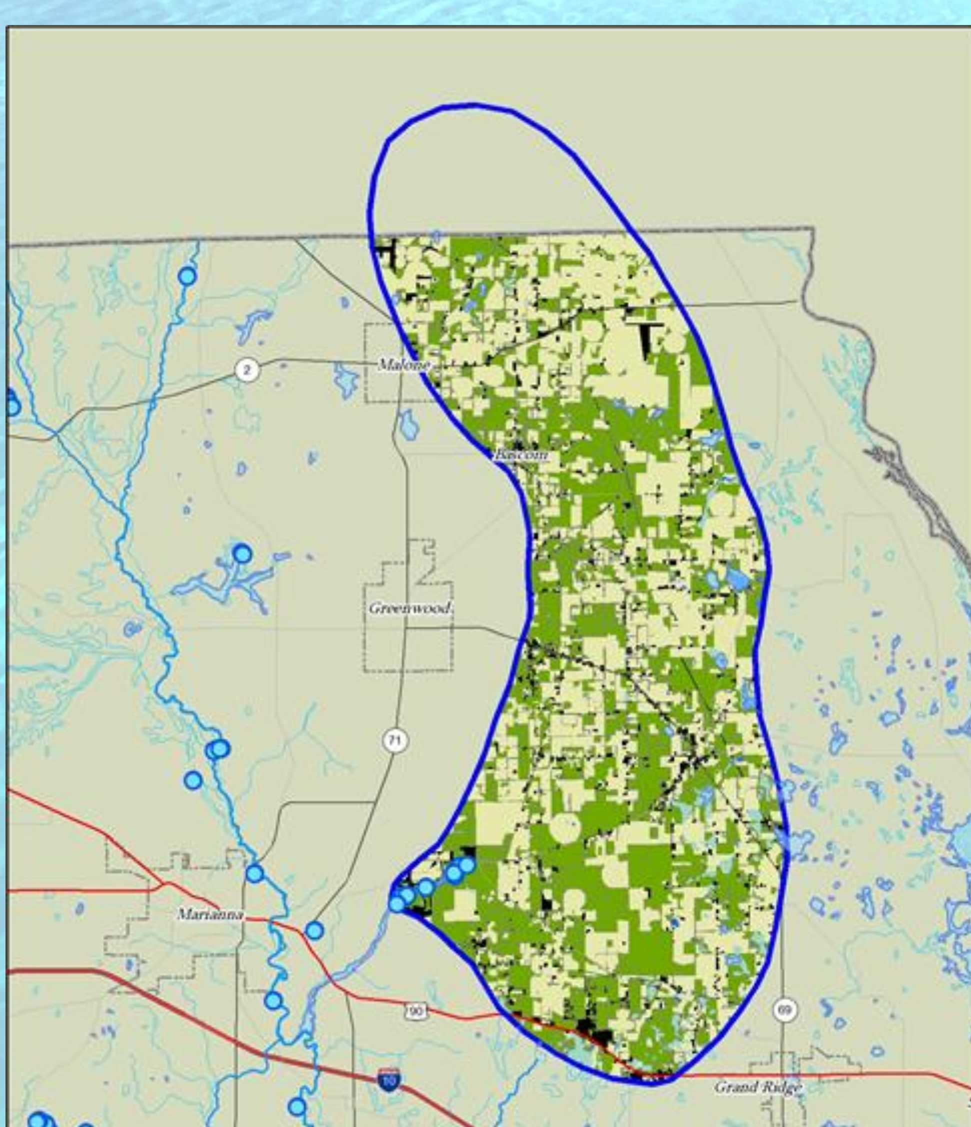
Nitrate Sources of Springs Discharging to Merritt's Mill Pond, Jackson County, Florida

Technical File Report 2011-01



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Introduction

Merritt's Mill Pond, located in Jackson County, has been a popular destination for generations of area residents. The Mill Pond forms the headwaters Spring Creek, a tributary to the Chipola River. As its name implies, Spring Creek flow results from the discharge of numerous Floridan Aquifer springs and seeps, including one first-magnitude spring – Jackson Blue. Merritt's Mill Pond was originally created by the impoundment of upper Spring Creek about 1.5 miles south of the headsprings. The current level and extent of the pond was formed in the 1920's during the construction of U.S. Highway 90.

Springs in Florida have been an important bellwether for environmental change since they integrate the anthropogenic impacts on ground water over large areas. Like many other springs, Jackson Blue has seen a significant increase of nutrient concentrations with corresponding degradation of native spring ecosystems. Previous studies have identified the predominant source of nutrients in Jackson Blue Spring as inorganic fertilizer. At an average of 3.3 mg/L, Jackson Blue Spring has the second highest nitrate concentration of the first-magnitude springs in the state.

In 2002, the NWFWMD completed a study of land use and nutrient loading in the Jackson Blue Spring Basin. The District also measured water levels and interpreted a Floridan Aquifer potentiometric surface to determine the Jackson Blue Spring ground water contribution area (Chelette, et al. 2002). In 2004 the U.S. Geological Survey (USGS) published a report on regional ground water flow in the Lake Seminole area (Jones and Torak 2004). The study included a Floridan Aquifer potentiometric surface similar to the NWFWMD surface. In both cases, the ground water contribution area for Jackson Blue Spring approximated a tear-drop shape extending north to just above the Florida-Alabama state line. The USGS also completed an analysis of samples for stable isotopes and tritium from Jackson Blue Spring in 2001 as part of a larger work focused on estimating the ground water recharge age and nutrient sources for twelve first and second-magnitude springs located in Florida (Katz 2004). The analysis resulted in an estimated average ground water age of 17 years for Jackson Blue Spring with a nutrient signature indicating a source of predominantly inorganic fertilizer. The District completed a study of ground water quality in the Jackson Blue Spring basin and its relationship to water quality observed at Jackson Blue Spring (Barrios and DeFosset 2005). The study resulted in the delineation of a *principle contribution area* that corresponded with flow directions established in earlier reports.

This investigation was proposed to continue the study of springs located in Jackson County and address the following goals:

1) Identify and monitor all of the springs discharging to Merritt's Mill Pond and compare the water quality of the second-magnitude and smaller springs to the headspring (Jackson Blue) and to the water quality results obtained during the District's Jackson Blue Spring Basin sampling effort of October 2004,
2) Identify land use based on the 2004 digital orthophotographic data, compare the land use change from the 1994 data within the previously established ground water contribution area for Jackson Blue Spring, and determine if any spatial correlation exists between land use and water quality.
3) Create a detailed potentiometric surface of Northeast Jackson County to improve on previous efforts to delineate the spring basin.
4) Complete an isotopic analysis of the major springs to determine ground water age, recharge domain, and nutrient sources.

Merritt's Mill Pond Spring System

Merritt's Mill Pond

Merritt's Mill Pond was originally created in the late 1860's with the impoundment of Spring Creek by Coker Dam at a point located approximately halfway down the existing lake. In the 1920s, the mill pond was expanded to its current extent with the construction of the dam and weir at U.S. Highway 90. For most of the 20th century, the impoundment at US 90 was used as a small hydroelectric generation plant. During 1994-1996, the generator turbine was removed and the dam spillway and headwall were modified. Over the course of the pond's history, the water level has been drawn down five times for varying lengths of time: 1956, 1971-1972, 1980, 1990, and 1994-1996. With the exception of the 1994 and 1994-1996 drawdown events associated with the dam modification, the drawdowns have been for the purpose of maintaining or improving the aquatic health of the pond. Merritt's Mill Pond is renowned for its fishing, in particular redear sunfish (*Lepomis microlophus)* for which the pond holds the state record.

Merritt's Mill Pond measures approximately 4.25 miles in length from its headwaters at Jackson Blue Spring to the outfall into Spring Creek and has an average width of 500 feet. Depths are generally in the 10 to 12 foot range. Because of the water control structure, levels in the pond only fluctuate from 6 to 12 inches over the course of a year. The control structure at the pond outlet consists of a modified rectangular-notch weir over a liftgate that opens from the bottom (**Figure 1**). Although the outlet structure does have the capability of changing the water level in the pond, the structure has remained closed since the 1994-1996 drawdown event.

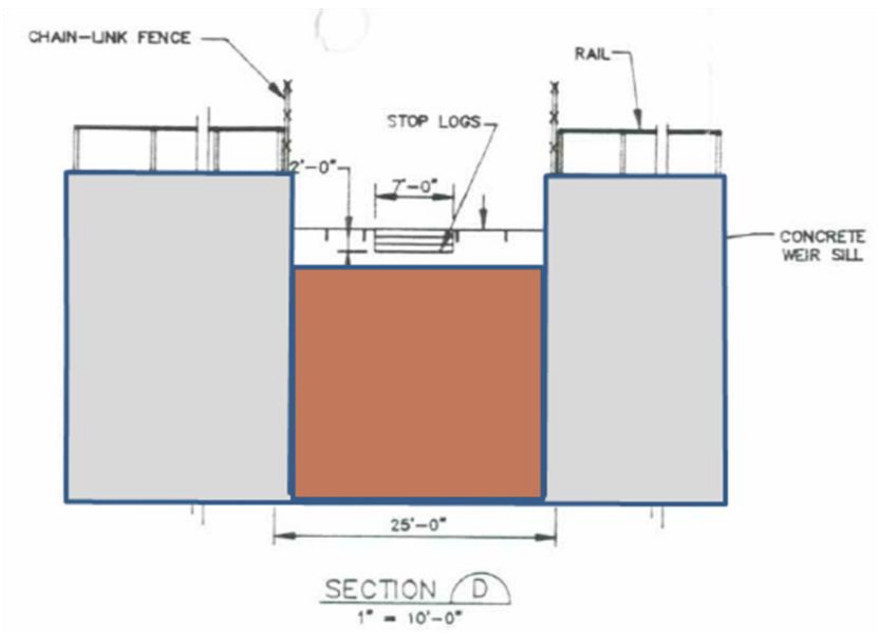

Figure 1. Merritt's Mill Pond Outflow Control Structure

Merritt's Mill Pond Springs

In September 2006, District staff, with the assistance of Edd Sorenson of Cave Adventurers, performed an inventory of both known and undocumented spring vents located in Merritt's Mill Pond. Eight springs were identified during the survey. The initial site reconnaissance included the collection of water quality field parameters (temperature, dissolved oxygen, pH, and Specific Conductance), differentially corrected GPS coordinates, and site photographs. Spring descriptions are detailed in **Appendix A**. **Figure 2** displays the locations of the springs within Merritt's Mill Pond. The period of October 2006 to December 2007 was one of the driest on record with Jackson County under severe drought conditions for much of the year. As a result, two of the springs previously reported flowing – Indian Washtub and Lamar's Landing – did not appear to have measurable discharge. Field parameters measured at these sites may have water quality more indicative of the

Mill Pond than ground water. As a result of the survey, six springs were selected for isotopic analysis and quarterly water quality monitoring: Jackson Blue, Shangri-La, Twin Caves, Hole-in-the-wall, Heidi Hole, and Gator Hole.

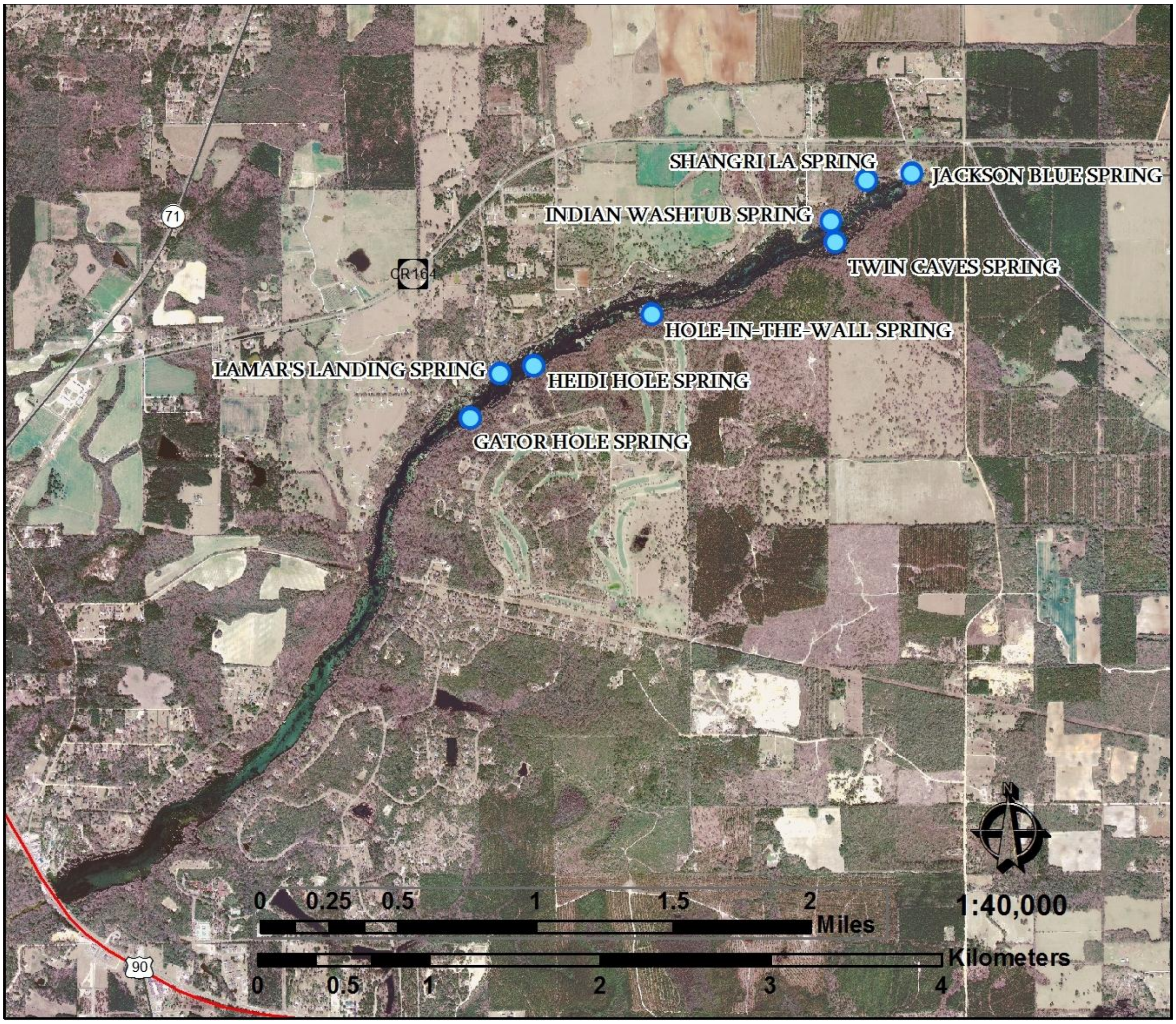

Figure 2. Floridan Aquifer Spring Locations, Merritt's Mill Pond

Hydrogeology

The springs of Merritt's Mill Pond are located within the Dougherty Karst Plain District, which encompasses the northern portions of Bay and Calhoun counties, all of Jackson County and the majority of Washington and Holmes counties. In this region, the Floridan Aquifer is recharged through the overlying Intermediate System and discharges to springs and rivers. The rate of recharge is estimated at 12 to 18 inches per year overall for the springs recharge basin. Given the near absence of surface drainage in the basin, this amount is essentially the Remaining precipitation after accounting for evapotranspiration. The semi-confined condition of the Floridan Aquifer across the Dougherty Karst Plain allows for large amounts of local recharge, but also makes the Floridan Aquifer especially vulnerable to contamination from activities occurring on the land surface.

In Jackson County, the Floridan Aquifer is comprised of the Chattahoochee Formation, the undifferentiated Marianna/Suwannee Limestone, and the Ocala Limestone (Scott, 1993; Campbell, 1993). The region is characterized by a thin, generally less than 50-ft thick Intermediate System confining unit that is often absent or breached by sinkholes. The Floridan Aquifer itself is relatively thin, with a thickness of approximately 100 feet in north Jackson County, where it is composed only of the Ocala Limestone (Moore 1955). Continuing south to the Jackson County – Calhoun County line, the Floridan Aquifer thickens to approximately 500 feet with the occurrence of the younger limestone formations (Pratt et al. 1996)

Springshed Delineation

Previous efforts at springshed delineation for Jackson Blue Spring relied on land surface elevations derived from USGS topographic maps. The accuracy of topographic data is sufficient for the production of a potentiometric surface with a contour interval of ten feet. The goal of the springshed refinement was to improve the accuracy of the vertical datum to approximately one foot, allowing for an improved understanding of flow directions within the study area. To this end, land surface elevations were determined utilizing both instrument survey and LiDAR (**Li**ght **D**etection **A**nd **R**anging) elevation models. In March 2007, a total of seventy-seven observation, domestic and public supply wells were used as measurement locations to determine the depth of water. Water measurements were conducted with an electronic water level indicator or steel tape, both with a measurement accuracy of 0.01-foot. The water level measurements were combined with land surface elevation data to arrive at the elevation (in MSL, NAVD) of the Floridan Aquifer potentiometric surface. The resulting refined Floridan Aquifer Potentiometric surface and springshed delineation are presented in **Figure 2**. Spring basins are variable in nature due to changes in hydraulic head levels, rainfall, and aquifer use, therefore the springshed presented below provides a snapshot of conditions present in March 2007.

Spring Discharge

Discharge measurements at Jackson Blue Spring range from a low of 28.1 cubic feet per second (cfs) in September 2007 to a high of 305 cfs in April 2003. The average discharge at Jackson Blue Spring is 116 cfs based on 76 field measurements collected by both the USGS and the District during December 2001 through December 2009.

District staff measure the discharge at Jackson Blue Spring and the discharge downstream of the Merritt's Mill Pond impoundment on Spring Creek. The difference between the two measurements represents the additional discharge contributed to Merritt's Mill Pond from the other sources in the system. These other sources primarily reflect flow contributions from other smaller springs within Merritt's Mill Pond. The additional spring discharge ranged from a low of 6.7 cfs in January 2008 to a high of 142 cfs in June 2009. Measurements were timed to avoid rainfall events to eliminate the added discharge contributed to the Mill Pond from local surface water runoff.

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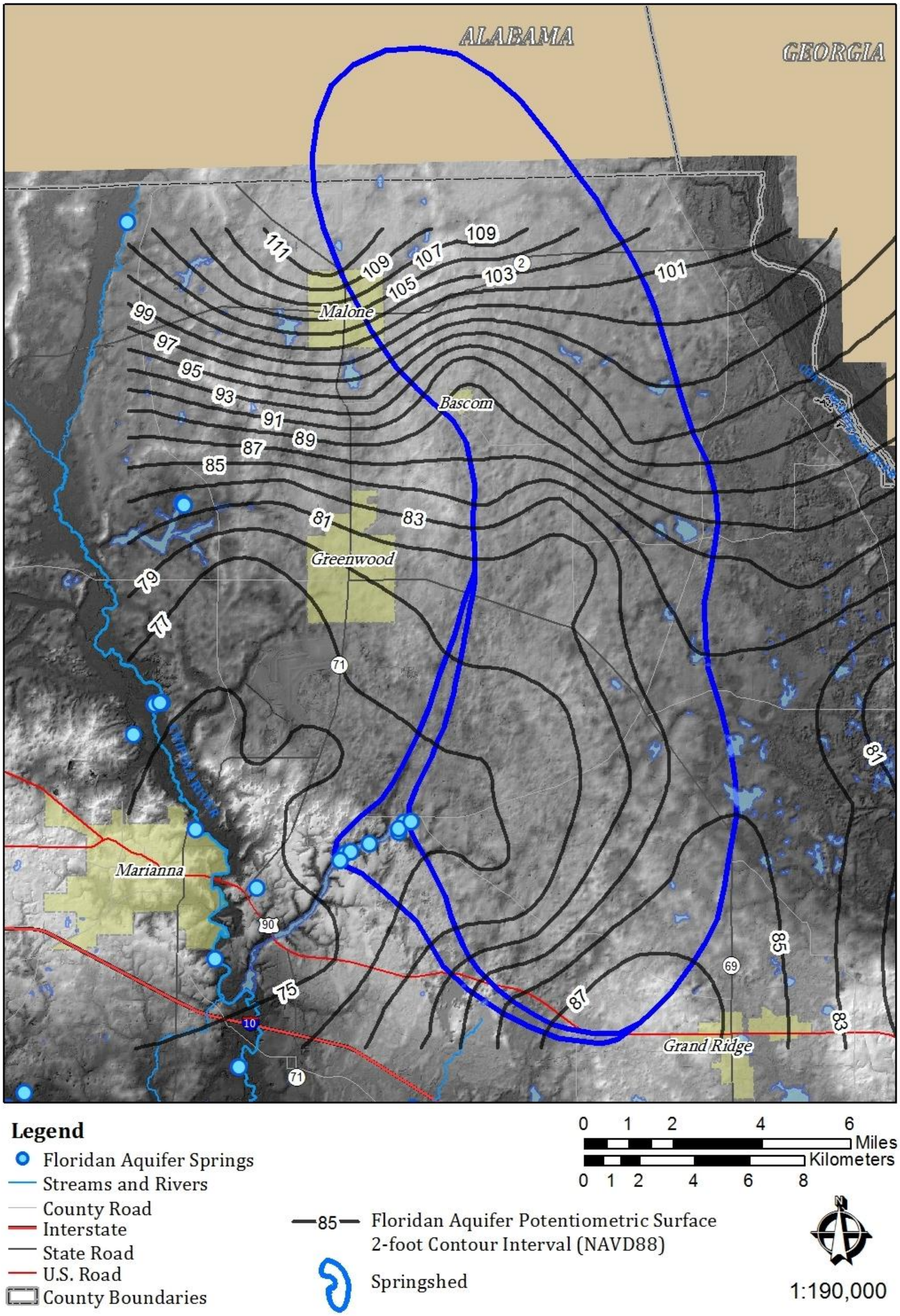

Figure 3. Merritt's Mill Pond Spring Basin Delineation

In June of 2007, the District contracted with Karst Environmental Services (KES) to conduct submerged discharge measurements within the exit conduits of six spring vents located in Merritt's Mill Pond. These measurements were conducted once at each spring during July 2007. In most cases, conventional discharge measurements are not obtainable due to the lack of a confined channel, the presence of diffuse discharge, or the presence of aquatic vegetation. **Table 1** summarizes the results. The total measured spring discharge was 49.64 cfs. In comparison, the measured outflow from Merritt's Mill Pond was 56.3 cfs. Thus, Jackson Blue Spring contributed approximately 69% of the total flow, the minor springs contributed 14%, and the remaining 17% was from other unmeasured sources. Based on measurements of discharge and pond outflow taken during 2006-2010, Jackson Blue Spring accounts for 70% of the pond outflow on average (**Figure 3**).

Table 1. Submerged Spring Discharge Measurements

Spring	Date	Depth (ft)	Discharge (cfs)
Jackson Blue Spring	7/16/2007	8-20	39.1
Shangri-La Spring Main	7/18/2007	7-10	3.69
Shangri-La Spring Fissure	7/20/2007	18	0.18
Shangri-La Spring Total	-	-	3.87
Twin Caves Spring	7/19/2007	14-20	1.60
Hole-In-The-Wall Spring	7/17/2007	35-36	1.28
Heidi Hole Spring	7/20/2007	22-23	0.16
Gator Hole Spring	7/20/2007	13-17	0.93
Total			49.94

In December 2004, the District installed a ground-water level recorder within a Floridan Aquifer well located in the Jackson Blue Spring basin to determine if a relationship exists between the ground-water level in the Floridan Aquifer and measured Blue Spring Discharge. A well (NWFID# 5266) meeting construction, access and location requirements was found near the center of the Jackson Blue Spring basin in Two Egg, approximately 5.7 miles from the spring vent. **Figure 4** displays ground-water levels and the 56 spring discharge measurements collected since December 2004. As can be seen on the graph, there is a significant correlation between spring discharge and the ground-water level; enough so that the data can be used to develop a rating curve to estimate spring discharge. The District has created a discharge rating for Jackson Blue Spring based on this relationship (**Figure 5**). The rated discharge hydrograph is displayed as **Figure 6**. Summary statistics for Jackson Blue spring flow are given in **Table 2**.

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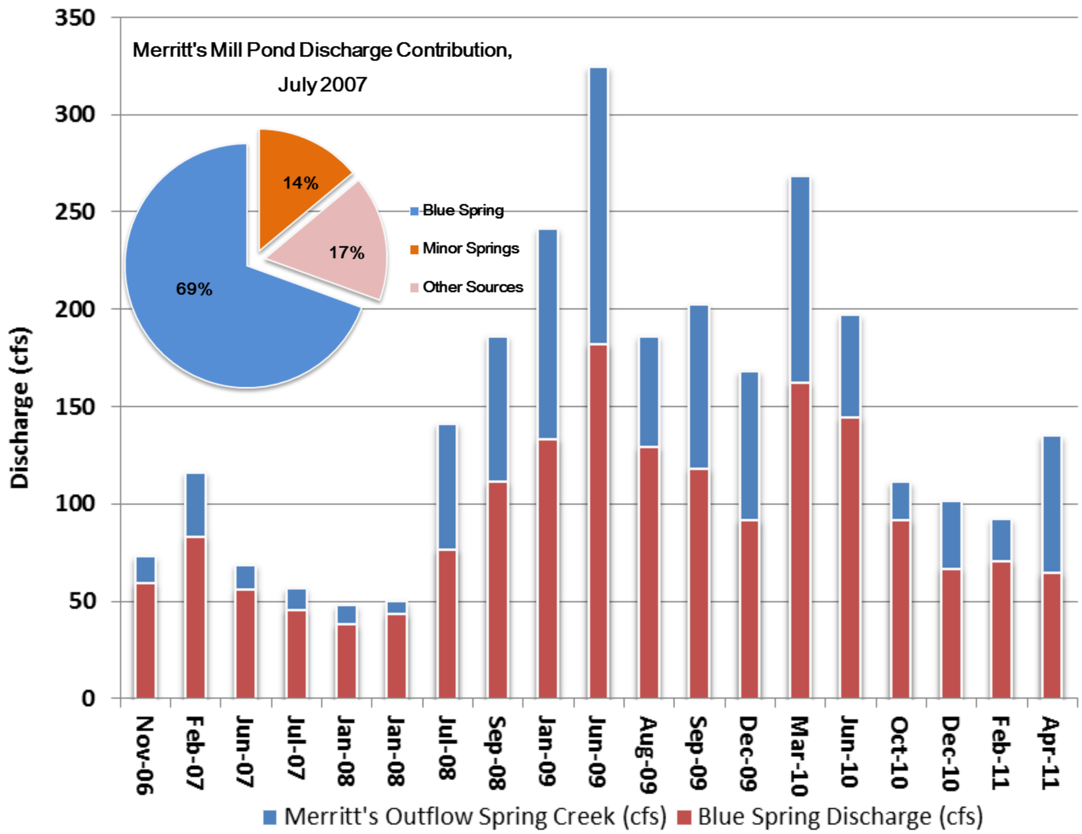

Figure 4. Contribution of Jackson Blue Spring to Merritt's Mill Pond Discharge

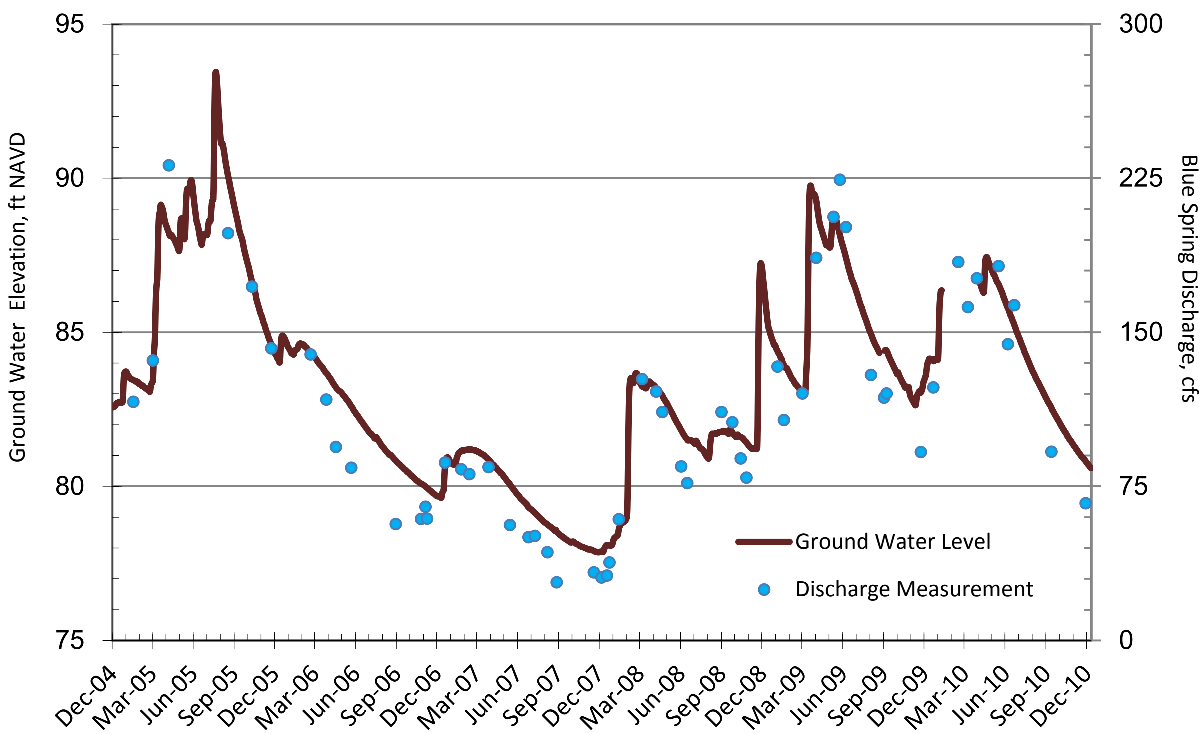

Figure 5. Discharge measurements and ground water levels measured at the Pittman well

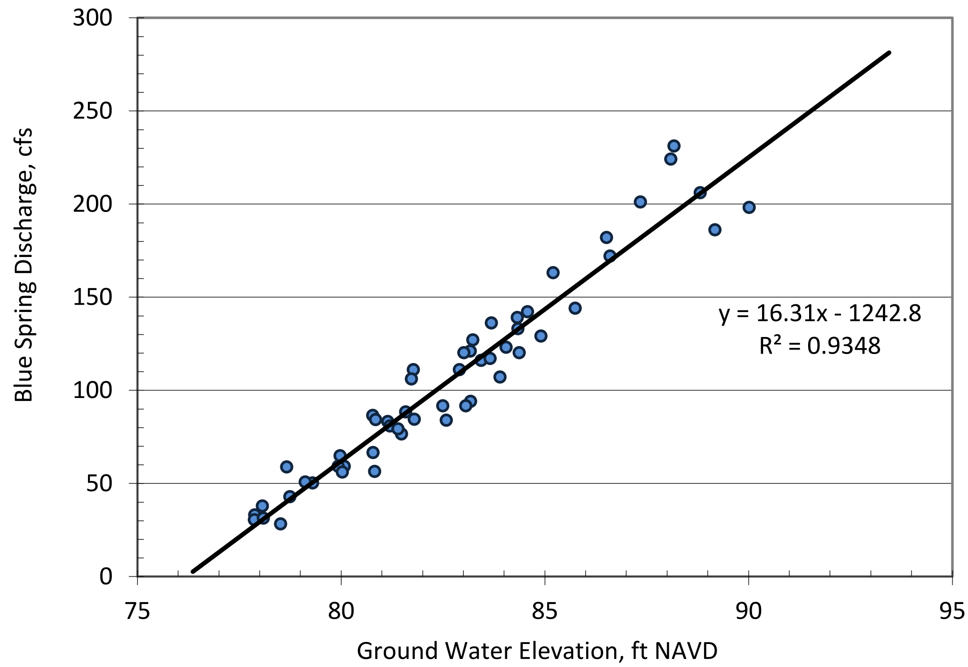

Figure 6. Ground water level-discharge relationship for Jackson Blue Spring

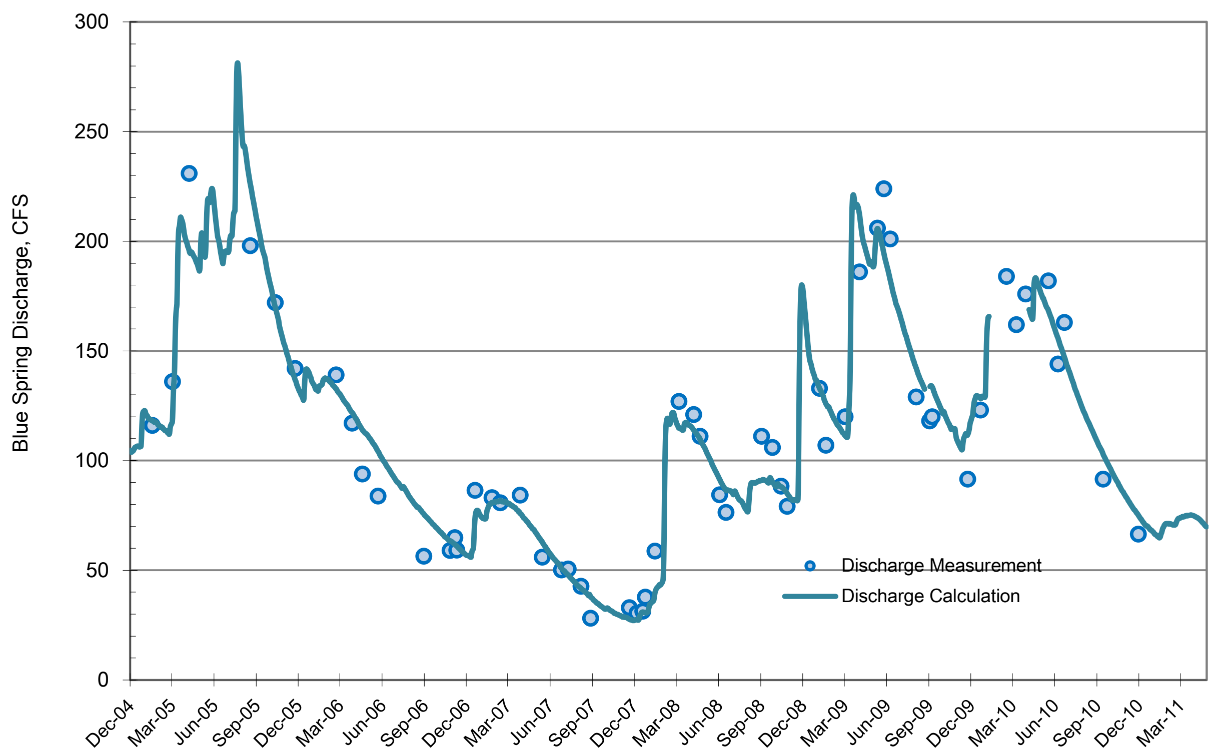

Figure 7. Time Series Plot of Blue Spring Discharge, 12/21/2004-05/31/2011

Table 2. Jackson Blue Spring Summary Discharge Statistics (cfs)

Mean	113
Median	110
Minimum	28
Maximum	283
90% exceedance	44
80% exceedance	69
70% exceedance	81
60% exceedance	90
50% exceedance	110
40% exceedance	118
30% exceedance	132
20% exceedance	158
10% exceedance	196

In 2003, the USGS installed a pond level monitoring station located near Jackson Blue Spring with funding provided by the Florida Department of Environmental Protection. At the time, the monitoring site was installed under the hypothesis that the Mill Pond stage was primarily determined by the volume of flow discharged from Jackson Blue Spring. **Figure 8** compares the pond stage and measured spring discharge from 2003 through 2009. The stage data collected to date indicates that Jackson Blue Spring discharge is a substantial factor in determining pond level; however, enough variability is contributed by other factors which make the development of a rating curve based on pond stage problematic. Therefore, the District recommends that the ground water level – discharge relationship be used instead as the basis for estimating the discharge from Jackson Blue Spring.

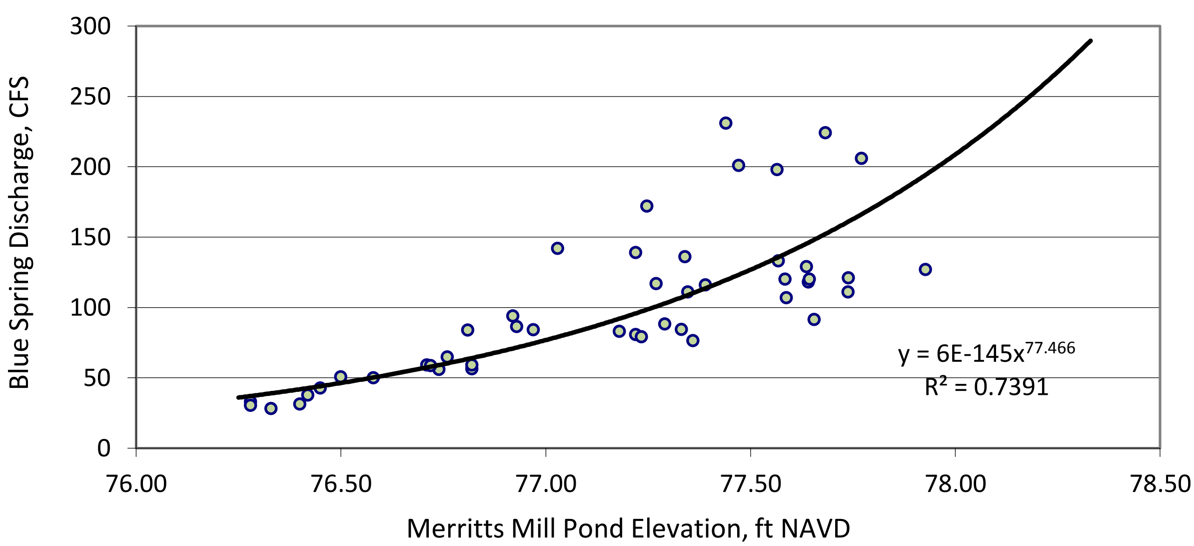

Figure 8. Merritt's Mill Pond Elevation and Measured Spring Discharge

Land Use in the Merritt's Mill Pond Spring Basin

Jackson County has traditionally been one of Florida's most productive agricultural communities. In 2002 the county ranked first in the state for cotton, peanut, and wheat acreage (FASS 2002). Unfortunately the agricultural success of the county has had an adverse impact on water quality at many of the springs in the area. As noted previously, the analysis of stable nitrogen isotopes at Jackson Blue Spring has concluded that the elevated nitrate values in the spring are predominantly due to the leaching of manufactured fertilizer into the aquifer within the spring's contribution area. Within the past decade, development pressures have become increasingly commonplace in the Panhandle and Jackson County is no exception. Residential and commercial developments have the potential of impacting ground water quality through wastewater disposal and stormwater runoff. A change from agricultural to developed land use in the Jackson Blue Spring Basin could influence water quality and quantity at the spring. The purpose of this analysis is to identify the land use change from 1994 to 2004 and to determine if any correlation exists between the 2004 land use and changes of ground water quality during this period.

Methodology

The study period of 1994 to 2004 was selected due to the availability of digital aerial photography. Land use can be easily delineated into general categories using photographic interpretation. An analysis of land use based on the 1994 data was completed by the District in 2001. To create the 2004 dataset, District staff used a GIS file containing the Jackson County Property Appraiser parcel data. This shapefile contained attributes identifying the zoned land use for each parcel. Using GIS, District staff compared each parcel, numbering approximately 3000 in the delineated spring basin, to its aerial image. The parcel data was then subdivided, if necessary, into land use components. For the purposes of this study, land use was classified using the Level I categorization recognized by the USGS (Anderson et al 1976). This classification uses generalized interpretation that is applicable to a study of transition from a non-developed to a developed state. As a result, six categories of land use were defined in the spring basin:

1. Built-up Land – This includes commercial property, residential property, churches and associated adjacent land such as parking lots and yards.
2. Agricultural Land – Land used for production of food or commercial/industrial material including row crops, center pivots, and pasture.
3. Open Land – Includes borrow pits and cleared areas with no discernable future use.
4. Forest Land – Any area not associated with a higher impact land use with a tree canopy cover greater than 10 percent.
5. Wetland – Forested or unforested wetlands delineated by the National Wetlands Inventory.
6. Water – Any area with visible standing water.

It is important to note that there are errors, both in interpreting the aerial data and in processing polygon attributes in GIS, which may account for slight changes in the land use totals. However, the data was subjected to review by several experienced District staff and each parcel was verified at least once by another analyst.

Results

The results of the 2004 land use analysis and comparison with 1994 data are listed in the **Table 2**. A map of the 2004 landuse is included in **Figure 11**. The Jackson Blue Spring Basin, as delineated in 2001, comprises approximately 69,000 acres. In comparison with 1994, the 2004 data remains essentially unchanged with respect to Wetland and Water. Agricultural Land increased slightly while Barren Land and Built-up Land increased significantly. There was a substantial decrease in Forest Land. While still

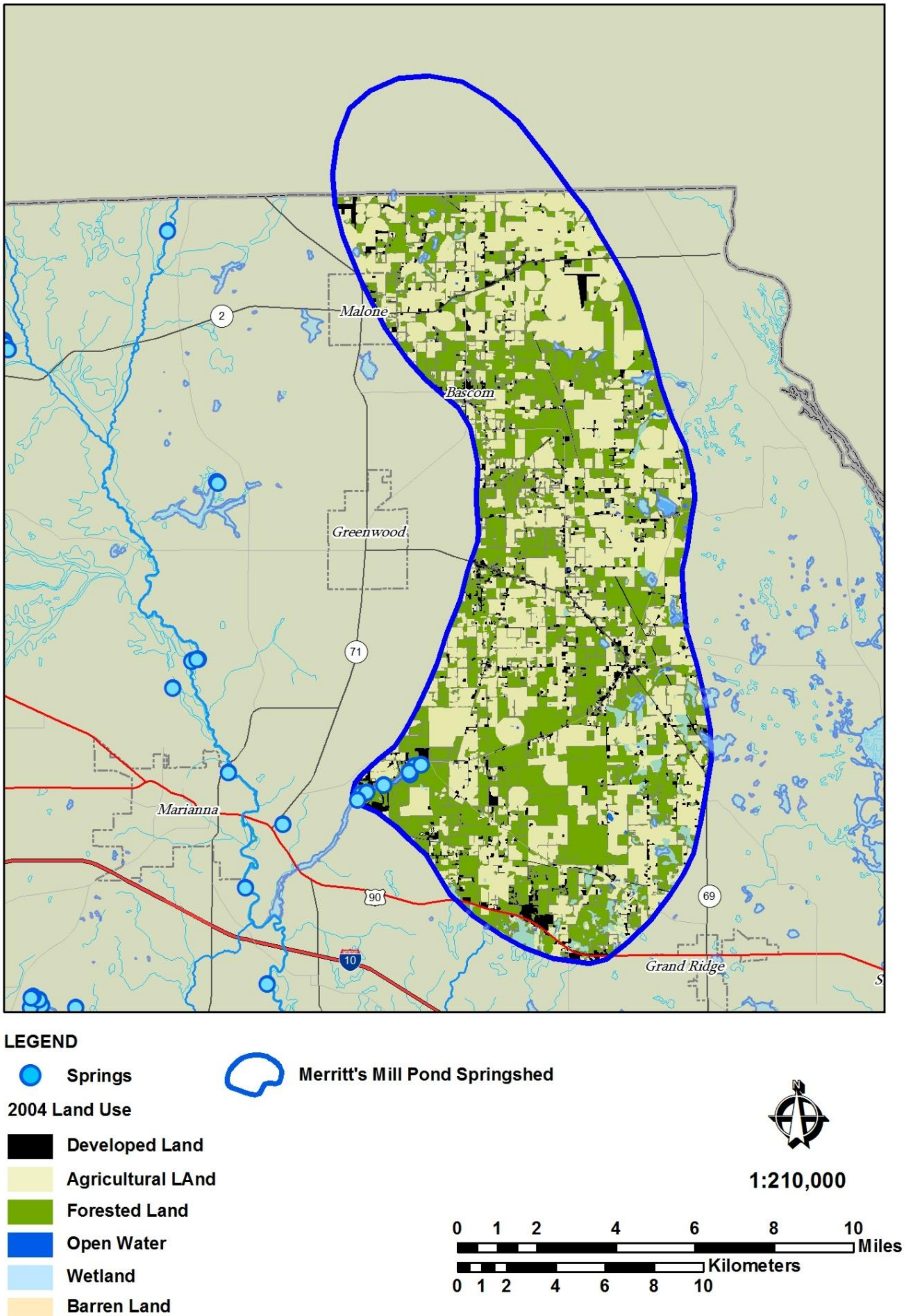

Figure 9. Land Use in the Jackson Blue Springshed

Table 3. Land use change from 1994 to 2004 in the Jackson Blue Spring Basin

Land Use Category	Acreage 1994	2004	Change in Acreage	% Change
Agricultural Land	33,410	33,938	528	2%
Upland Forest	31,005	28,765	-2240	-7%
Developed Land	2,095	3,794	1699	81%
Wetlands	1,662	1,663	1	0%
Water	215	215	0	0%
Open Land	113	198	86	76%

comprising a minor portion of land use in the study area, the increase of Built-up Land by 1699 acres came at the expense of Forest Land. The increase in Open Land can be attributed to the harvesting of pine plots as well as the clearing of land for other uses.

The land use analysis does not indicate that developed land is replacing agricultural land in the Jackson Blue Spring basin. Instead, over the ten years between the snapshots provided by the aerial photography, both land uses increased with a corresponding loss of forested land. The significance of this result is that the nutrient loading associated with both development and agriculture has likely increased as well.

Water Quality

Ground water quality within the Blue Spring Basin is defined by the properties of the geologic units comprising the Floridan Aquifer in the region as well as by the anthropogenic impacts associated with land use and water consumption. Generally speaking, the ground water in the Blue Spring basin is carbonate; its mineral components reflect the dissolution of the Ocala/Marianna Limestone sequence which forms the matrix of the aquifer in the basin. The District's chemical characterization of water quality in the basin, published in WRSR-0501, provides a detailed explanation of spatial variability of geochemistry in the springshed.

Based on the 2007 springshed refinement, approximately 80% of the Jackson Blue Spring Basin is located within Jackson County with an additional 20% located in southern Houston County, Alabama. The small size of the basin compared to other historic first magnitude springs in Florida supports the estimates of high intrabasin recharge. The USGS completed an analysis of samples for stable isotopes and tritium from Blue Spring in 2001 as part of a larger work focused on estimating the ground water recharge age and nutrient sources for twelve first and second-magnitude springs located in Florida (Katz 2004). The analysis resulted in an estimated average ground water age of 17 years for Blue Spring. The relatively young age of ground water discharging from Jackson Blue Spring is supported by high concentrations of dissolved oxygen measured both basin wide and in quarterly monitoring at Blue Spring.

Nitrate Concentration

The nitrate concentration measured at Jackson Blue Spring has increased from about 0.30 mg/L in the 1960's to the current value of 3.2 to 3.6 mg/L. As mentioned previously, this concentration is currently the second highest of Florida's first-magnitude springs; and, although relatively high, still well below the primary drinking water standard for nitrate of 10 mg/L. A time series chart displaying the increase in nitrate concentration over time is included in **Figure 10**. As depicted in **Figure 11**, the variability of nitrate concentrations during the recent interval falls within about 10% of the median value. This low variation is despite an order-of-magnitude difference between low and high discharge measured during the same period. The significance of this observation is that nitrate concentrations in the Blue Spring Basin are not subject

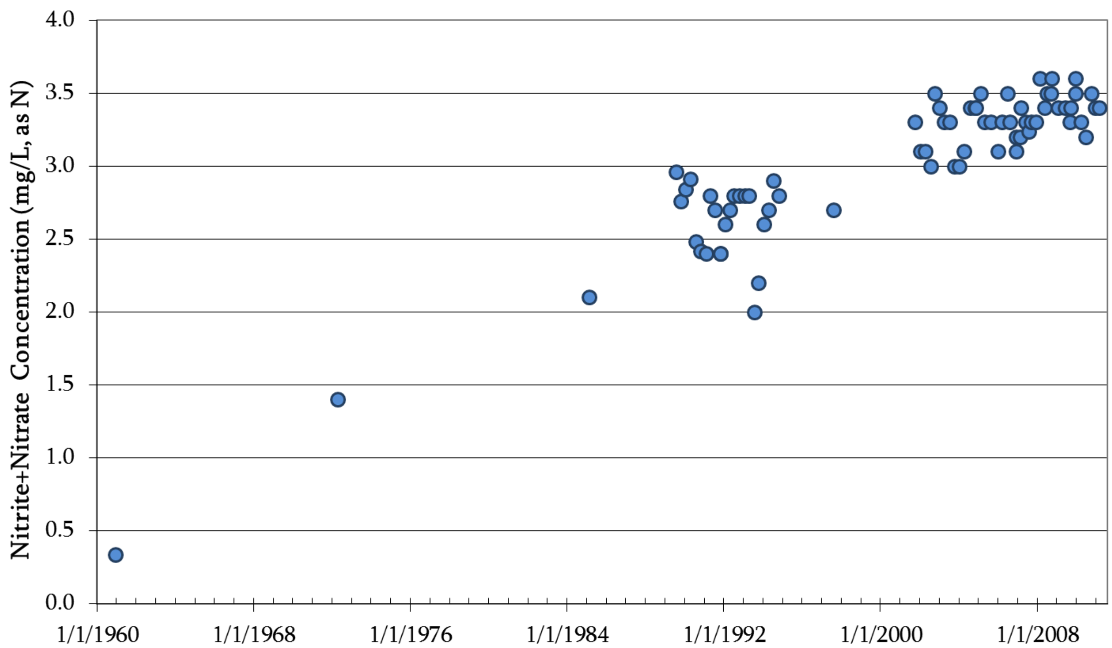

Figure 10. Blue Spring Nitrate Concentration: note increase in concentration from 1960-2010

to dilution during variable flow regimes and are therefore endemic to the aquifer. This conclusion is supported by sampling results for wells within and surrounding the spring basin. The source water for Blue Spring is consistently composed of ground water with relatively little or no attenuating influence from surface drainage into sinkholes or swallets. This also, in part, explains why the head difference between the upper basin and discharge point (the spring) serves as a viable proxy to discharge.

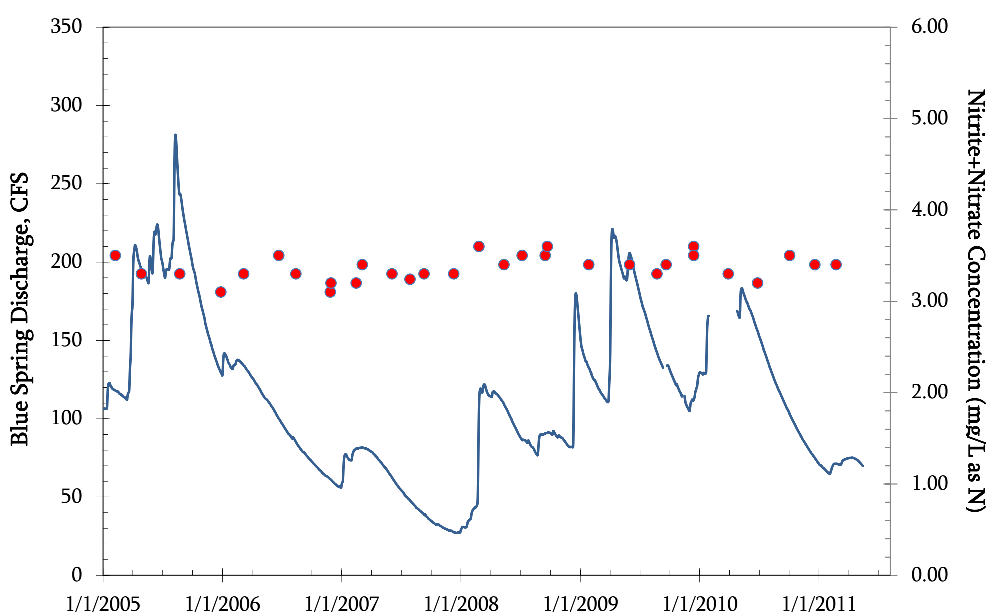

Figure 11. Discharge vs. Nitrite+Nitrate Concentration

The nitrate laboratory results for the other five springs sampled for this project are also elevated; ranging from a low of 1.2 mg/L at Twin Caves Spring to 4.0 mg/L at Shangri-La Spring (**Figure 12**). The complete laboratory results for the monitoring portion of this project are presented in the tables included in **Appendix B**.

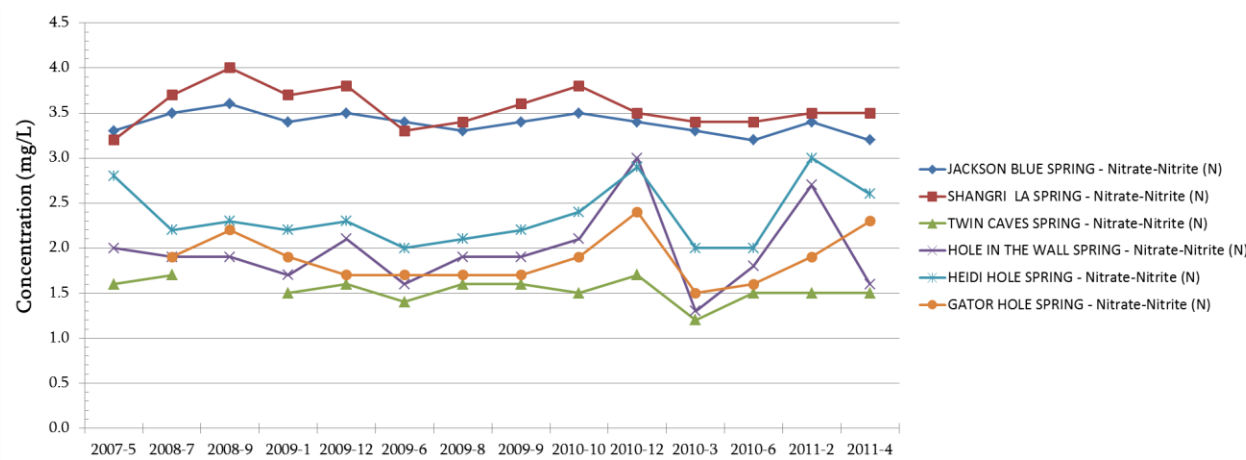

Figure 12. Nitrate Concentration, Merritt's Mill Pond Springs

Principle Components of Water Chemistry

In order to draw statistical conclusions on the springs' water chemistry, the mean water quality results from the 2007-2011 monitoring were combined with basin ground water quality data collected in 2004 and converted to *principle component scores*. The Principle Component Analysis (PCA) method is used to group the parameters into common components, or root causes of variability, within the sample population. The PCA is also useful in assisting with the clustering of similar samples and determination of the dominant chemical processes in the study area. The PCA used for this study was conducted in Microsoft Excel using methods established by Darlington (2004), Arsham (2006), Tyne, et al (2004) and Dalton and Upchurch (1978). Matrix and linear algebra operations for Excel were completed with the MATRIX.XLA add-in created by the Foxes Team at Calcolo Numerico (Volpi 2006). After normalization and standardization of the water quality variables, a correlation matrix was generated for the data set. The Jacobian eigenvalue and eigenvector matrices were then created. Components with eigenvalues satisfying Kaiser's criterion (eigenvalue >1) were retained and the associated eigenvectors were transformed into component loading coefficients. Varimax rotation was employed to concentrate variables within a single component. Component scores were then calculated for each sampling location by adding the products of the component loading coefficient and the standardized value for each variable.

Table 4. Jackson Blue Spring Basin Water Quality Principle Components

Principle Component	Primary Water Chemistry Variables	Indication	Spatial Trend
I	Conductance, pH, Alkalinity, Calcium, TDS	Ground water recharge through post-Eocene residuum sediments versus sands overlying Ocala Limestone	Increasing East to West
II	Dissolved O2, Magnesium, Sulfate, Fluoride	Hydrostratigraphy of the aquifer - Ocala Limestone versus Marianna/Suwannee/Ocala Limestone	Increasing North to South
III	Temperature, Phosphorus, Orthophosphate, Sulfate	Transition of the aquifer from the Ocala only to the Marianna/Suwannee/Ocala	Central Decreasing to North and South
IV	Nitrate-Nitrite, Potassium, Chloride	Influence of anthropogenic activities on water chemistry	Increasing South to North

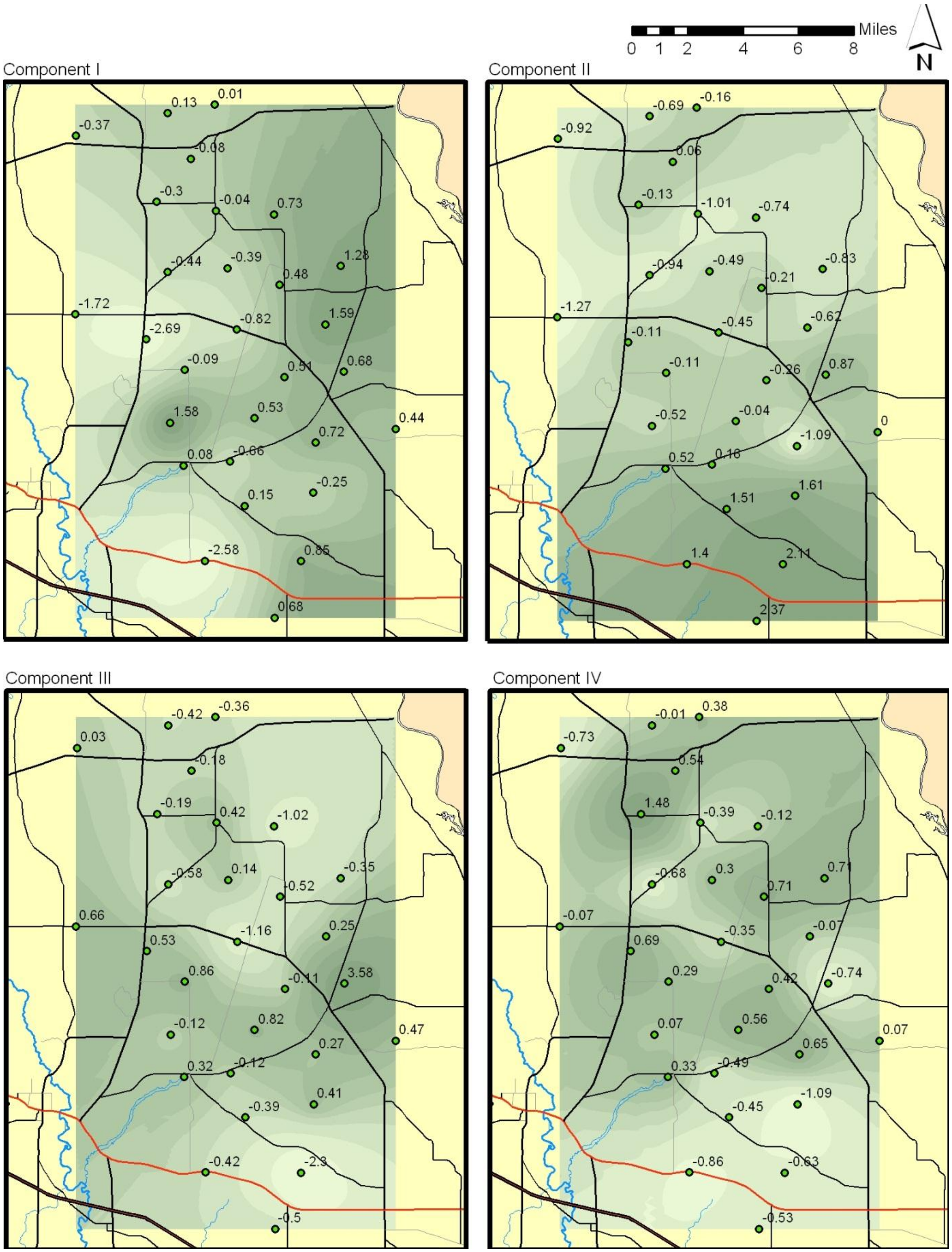

Figure 13. Spatial Trend of 2004 Principle Component Scores

In the 2005 PCA analysis, the authors concluded that four general influences, or *principle components*, determined the character of ground water chemistry in the Jackson Blue Spring Basin. The components were ranked from first through fourth in terms of contribution to the variability of the water chemistry data. **Table 4** summarizes the principle components and their significance. The six springs sampled for this project received component scores reflecting the influence of the principle components on water chemistry (**Table 5**). There is a spatial trend in the scores for three of the four components based on spring locations within Merritt's Mill Pond. These trends are of interest when differentiating the source of spring waters.

Table 5. Merritt's Mill Pond Springs Principle Component Scores

Spring Name	I	II	III	IV
Jackson Blue Spring	0.08	-0.12	0.25	0.37
Shangri-La Spring	-0.15	-0.10	0.51	0.49
Twin Caves Spring	-0.74	1.53	-0.15	0.06
Hole-in-the-Wall Spring	-0.84	1.15	0.18	0.66
Heidi Hole Spring	-1.32	1.26	0.99	0.85
Gator Hole Spring	-1.30	1.31	0.44	1.35

The Component I scores decrease proceeding downstream of the headspring: Jackson Blue and Shangri-La have low scores while Twin Caves, Hole-in-the-Wall, and Heidi Hole have progressively higher scores. This result indicates that the southwestern springs are receiving source waters from the western extent of the study area. Increasing Component II scores are attributed to higher concentrations of Magnesium, Sulfate, and Fluoride associated with the occurrence of the Marianna/Suwannee Limestone. With elevated Component II scores, Heidi Hole, Hole-in-the-Wall, and Twin Caves are therefore receiving source water influenced by the hydrostratigraphy in the southern extent of the study area while Jackson Blue Spring and Shangri-La appear to have source waters associated with the northern Eocene residuum and Ocala Limestone. Only one spring, Heidi Hole, has a significantly different score for Component III. This would indicate source waters originate in the central region of the study area. The Component IV scores show a clustering trend, with Jackson Blue Spring and Shangri-La both displaying mid-range values, Twin Caves relatively low, and the three southern springs then increasing proceeding downstream. The high Component IV scores for Hole-in-the-Wall, Heidi Hole, and Gator Hole are primarily caused by increases in Potassium and Chloride concentrations despite modest reductions in Nitrate-Nitrite. The springs are also located in proximity to residential development, including a golf course subdivision, and may be more influenced by wastewater treatment in addition to fertilizer application.

The results of the principle component analysis suggest that for springs located further downstream of Merritt's Mill Pond, there is a source of water that increasingly, if not solely, originates in the southern and eastern extent of the larger groundwater contribution area. The results of the principle component analysis also agree with flow directions based on the refined potentiometric surface of Northeast Jackson County (**Figure 3**). Clearly, not all of the springs in Merritt's Mill Pond share a common springshed. Jackson Blue and Shangri-La springs appear to discharge ground water originating from a larger area that incorporates more variability in ground water chemistry. Ground water from Twin Caves, Hole in the Wall, and Heidi Hole springs appears to originate from more limited areas that represent sub-basins within the more extensive and traditionally understood Jackson Blue springshed.

Sources of Spring Discharge

The analysis of stable and radiologic isotopes and dissolved gas in ground water can provide significant insight into the sources of spring discharge; including recharge condition, ground water age, and nutrient sources. A previous analysis of stable nitrogen isotopes at Jackson Blue Spring revealed that elevated nitrate values in the spring are predominantly due to the leaching of manufactured fertilizer into the aquifer within the spring's contribution area (Katz 2004). The USGS also concluded that the average recharge age of ground water discharge from Jackson Blue Spring was approximately 17 years. In July 2008, the District completed a round of stable isotope, dissolved gas, and tritium sampling from six springs in the Merritt's Mill Pond spring group, including Jackson Blue Spring. The additional data could be used to verify the findings published by the USGS for Jackson Blue Spring and collect additional information on the smaller springs.

Age and Residence Time of Spring Water

Dissolved gas data collected from springs are useful in determining the recharge conditions within the spring basin as well as assisting in the assessment of denitrification or other processes that can alter gas concentrations. The solubility of dissolved gas increases greatly with decreasing water temperature. It can be concluded that ground water with dissolved gas concentrations in equilibrium with the atmosphere under local ambient temperature conditions generally has a local recharge area. The recharge temperature and atmospheric equilibrium can be evaluated using a plot of dissolved Argon versus dissolved Nitrogen gas concentrations (Busenberg et al. 1993) presented in **Figure 14**. **Table 6** displays the dissolved gas, recharge temperature and excess air results from the six springs sampled for this project.

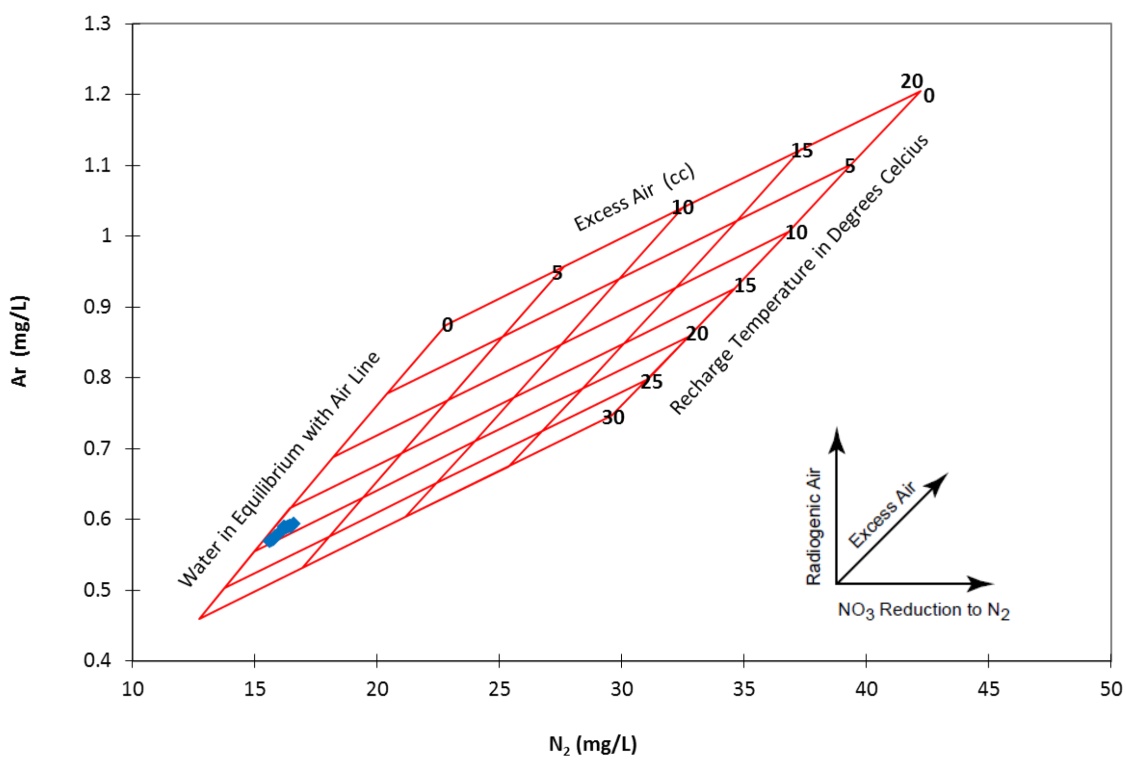

Figure 14. Dissolved N2 vs Argon Plot: Gas Concentration Normalized to Sea Level

The concentrations of N_2 and Argon samples plot very close to the atmospheric equilibration line with very low amounts of excess air added during recharge or as a result of sampling methodology. The amount of excess air calculated from measured concentrations varies from a low of 0.7 cc to a high of 1.4 cc (both at STP). There is a very minor shift to the right, indicating little to no denitrification occurring during recharge or within the aquifer. This result is significant because it leads to the conclusion that the recharge rate is high enough that pore water is not retained long enough in the soil horizon for bacteria to contribute appreciably to denitrification. Also, there is no evidence of radiogenic enrichment of Argon, but since there are few terrigenous sediments in the basin, this is no surprise.

Table 6. Dissolved Gas Data, Excess Air Calculation, and Recharge Temperature

Sample Name	Field Temp °C	N_2 mg/L	Ar mg/L	O_2 mg/L	CO_2 mg/L	CH_4 mg/L	Excess Air cc	Recharge Temp °C
Jackson Blue Spring (a)	20.6	16.228	0.586	6.637	5.704	0.000	1.05	18.6
Jackson Blue Spring (b)	20.6	16.163	0.586	6.658	5.615	0.000	0.92	18.4
Shangri-La Spring (a)	20.6	16.077	0.582	6.647	6.100	0.000	0.97	18.8
Shangri-La Spring (b)	20.6	16.028	0.580	6.735	6.107	0.000	0.96	19.0
Twin Caves Spring (a)	20.3	16.423	0.587	5.400	10.128	0.117	1.33	18.9
Twin Caves Spring (b)	20.3	16.548	0.591	5.402	10.165	0.066	1.41	18.7
Gator Hole Spring (a)	20.0	15.707	0.570	5.567	10.859	0.034	0.84	19.7
Gator Hole Spring (b)	20.0	15.793	0.574	5.452	10.813	0.043	0.82	19.3
Hole in the Wall Spring (a)	20.1	16.303	0.587	4.952	9.813	0.003	1.16	18.7
Hole in the Wall Spring (b)	20.1	16.397	0.588	4.964	10.026	0.002	1.27	18.8
Heidi Hole Spring (a)	20.7	15.582	0.567	5.722	13.349	0.008	0.72	19.8
Heidi Hole Spring (b)	20.7	15.637	0.568	5.745	13.634	0.011	0.79	19.8

The apparent recharge temperatures range from a low of 18.4 °C at Jackson Blue Spring to a high of 19.8 °C at Heidi Hole Spring. Both results are very close to the average annual air temperature of 18.9 °C at the NWS Chipley, FL weather station, and well within the error of measurement of +/- 3 °C. Divergent temperatures would indicate remote recharge in a different latitude or under paleoclimate conditions. Thus, the temperature results verify that recharge to the Floridan is occurring locally under current climate conditions.

Table 7. Results of Hydrogen, Oxygen, and Nitrogen Stable Isotope Analysis

Station Name	Delta ^2H x 1000	Delta ^{18}O x 1000	Delta ^{15}N x 1000	Mean Nitrate (mg/L) 2007-2011
Jackson Blue Spring	-19.44	-3.9	2.43	3.39
Heidi Hole Spring	-17.84	-3.94	2.3	2.35
Hole in the Wall Spring	-18.66	-3.89	2.81	1.96
Shangri La Spring	-19.41	-3.9	3.07	3.56
Twin Caves Spring	-19.01	-3.88	3.74	1.53
Gator Hole Spring	-18.08	-3.87	3.7	2.36

Stable isotopes of oxygen (Delta ^{18}O) and hydrogen (Delta ^2H) were used to determine the source water and characterize possible mixing of water from different sources. The oxygen and hydrogen isotopes measured in the springs of Merritt's Mill Pond are located near the Global Meteoric Water Line (GMWL) (Craig 1961) and in line with the regional meteoric water line determined by the USGS (Katz 1995). The results indicate that the springs are recharged from rainfall that is not subject to evaporative processes, bypasses the surface water phase, and proceeds directly to ground water. The area of Jackson County identified as the spring recharge basin has very few surface water features and is notable for the blank area expressed by the National Hydrologic Database (NHD) map coverage.

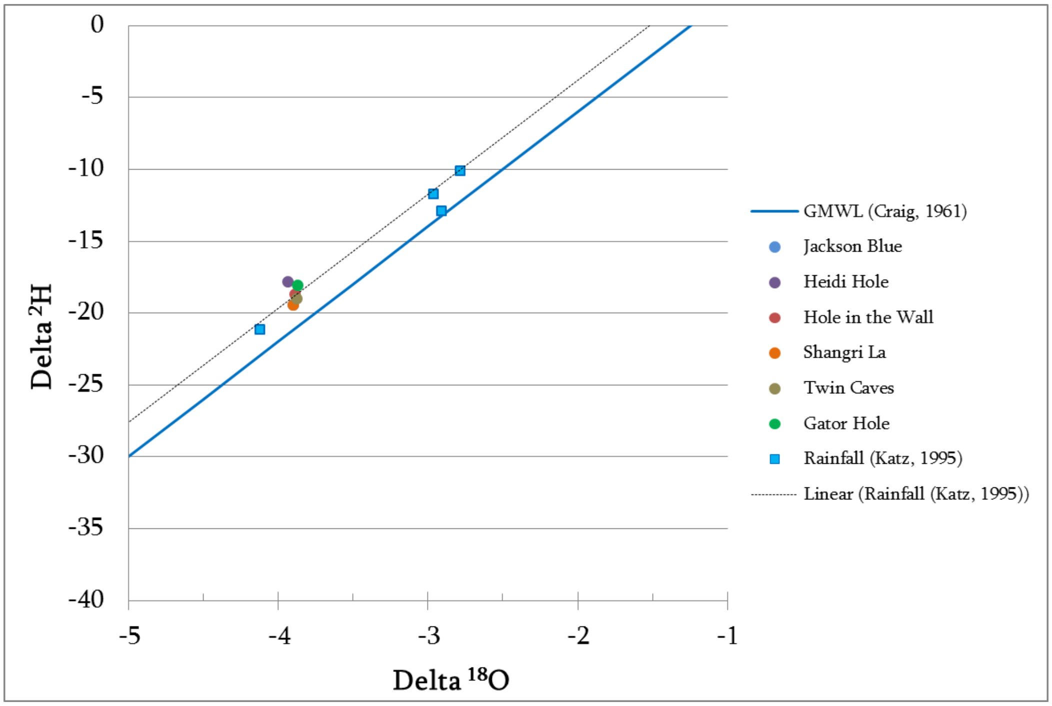

Figure 15. Stable Isotopes of Oxygen and Hydrogen Plotted Against the Global Meteoric Water Line

The determination of ground water age using tracers such as chlorofluorocarbons (CFS) and tritium (^3H) is based on the assumption that detected concentrations have not been altered by biologic processes or influenced by air exchange after recharge. The previously reported results of the air-water equilibrium analysis indicate that air exchange is negligible and little to no biologic activity occurs after recharge. The presence of CFCs indicates that some fraction of the water in the aquifer was recharged after the widespread use of CFCs began in 1940 (Plummer and Busenberg 1999). Ground water discharge from springs integrates water from the various zones of the aquifer in the recharge basin and therefore represents a mean residence time. Due to the shallow karst nature of the Floridan Aquifer in the study area, a piston-flow model was used to determine the apparent age of water samples collected from the springs (Plummer et al 1998).

Concentrations of CFC-11, CFC-12, and CFC-113 in spring samples listed in **Table 8**, with few exceptions, do not yield consistent piston-flow ages. Most samples resulted with values greater than the maximum concentrations in the atmosphere and are listed as *contaminated*. Results listed as *Modern* are within the possible range of the modern atmosphere while *NP* indicates the sample was corrupted or breached in some manner. The combined data from the three CFCs can be interpreted in several ways; however, what data appears to be valid indicates an apparent age of waters mixing from modern to 20 years old. The high dissolved oxygen levels and low organic carbon levels should allow CFCs to be conservative in the aquifer, but because of the number of contaminated samples, CFC results may not be the most reliable metric for determining ground water age.

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Table 8. Springs CFC Results and Age Determination

Sample Name	Sampling Date	Time	Corrected concentrations IN SOLUTION CFC-12 pmol/kg	CFC-11 pmol/kg	CFC-113 pmol/kg	Model piston dates (excess air corrected) Dual dates are possible for CFC-11, CFC-12 & CFC-113 CFC-11 (1)	CFC-11 (2)	CFC-12 (1)	CFC-12 (2)	CFC-113 (1)	CFC-113 (2)
Jackson Blue-B	07/07/08	11:51	2.943	4.212	0.231	Contam.	Contam.	Contam.	Contam.	1987.0	NP
Jackson Blue-D	07/07/08	12:02	3.064	4.293	0.239	Contam.	Contam.	Contam.	Contam.	1987.5	NP
Shangri-La-B	07/08/08	9:36	2.465	3.840	0.397	Modern	Modern	Contam.	Contam.	Contam.	Contam.
Shangri-La-C	07/08/08	9:40	2.522	4.096	0.415	Contam.	Contam.	Contam.	Contam.	Contam.	Contam.
Twin Caves-C	07/08/08	12:41	3.770	6.021	0.198	Contam.	Contam.	Contam.	Contam.	1986.0	NP
Twin Caves-E	07/08/08	12:55	3.814	5.996	0.236	Contam.	Contam.	Contam.	Contam.	1987.5	NP
Twin Caves-A	07/08/08	12:26	3.862	5.958	0.236	Contam.	Contam.	Contam.	Contam.	1987.5	NP
Gator Hole-A	07/09/08	13:35	2.078	3.493	0.655	1991.5	1995.0	Contam.	Contam.	Contam.	Contam.
Gator Hole-E	07/09/08	14:16	2.077	3.638	0.692	1994.0	Modern	Contam.	Contam.	Contam.	Contam.
Heidi Hole-A	07/08/08	16:03	2.668	12.534	1.328	Contam.	Contam.	Contam.	Contam.	Contam.	Contam.
Heidi Hole-D	07/08/08	16:24	2.823	13.724	1.396	Contam.	Contam.	Contam.	Contam.	Contam.	Contam.
Heidi Hole-C	07/09/08	16:18	2.785	12.679	1.368	Contam.	Contam.	Contam.	Contam.	Contam.	Contam.
Hole in the Wall-D	07/09/08	10:32	2.162	3.759	0.972	1994.0	Modern	Contam.	Contam.	Contam.	Contam.
Hole in the Wall-E	07/09/08	10:39	2.195	3.371	0.979	1988.0	2005.0	Contam.	Contam.	Contam.	Contam.
Hole in the Wall-A	07/09/08	10:09	2.136	3.227	0.962	1987.5	2008.5	Contam.	Contam.	Contam.	Contam.

The tritium (^3H) concentrations measured in the spring samples ranged from 0.7 to 2.3 tritium units (TU) and indicate the passing of the ^3H tracer through the environment. Prior to atmospheric testing of nuclear fusion weapons in 1953, ^3H concentrations in the area were on the order of 0.2 TU or less (Thatcher 1962). Levels peaked in the 1960s at several hundred TUs as testing continued and then began dropping rapidly following the ban on atmospheric testing. The ^3H results (**Table 9**) demonstrate that spring recharge has occurred relatively recently but cannot be accurately determined due to the lack of a long-term record for the area. Additionally, the samples appear to be mixtures of very old waters (low R/Ra value) and relatively young waters (TU values > 1). Two age ranges are given for different assumptions of Rterr, necessary because of the high levels of ^4He measured in the samples. The calculated ages are weighted heavily by the younger component, so the age range shown should show preference to the younger component (Rigby 2008). However, the age ranges indicated agree with the ranges determined by other dating methods.

Table 9. Tritium (^3H) Sample Results

Sample ID	N2 (ccSTP/g)	Ar40 (ccSTP/g)	Kr84 (ccSTP/g)	Xe129 (ccSTP/g)	Ne20 (ccSTP/g)	He4 (ccSTP/g)	R/Ra	Tritium (TU)	Age using Ne (yr)	Age using EA (yr)	Excess Air (ccSTP/g)	Assumed Rterr
Jackson Blue-A	1.38E-02	3.31E-04	4.24E-08	2.77E-09	1.94E-07	1.81E-07	0.42	2.3	18.6	18.9	0.0035	1.8E-07
Jackson Blue-B	1.38E-02	3.31E-04	4.24E-08	2.77E-09	1.94E-07	1.81E-07	0.42	2.3	32.7	32.9	0.0035	2.8E-08
Shangri-La-A	1.35E-02	3.38E-04	4.16E-08	2.85E-09	1.94E-07	5.36E-08	1.04	2.3	11.1	11.2	0.0021	1.8E-07
Shangri-La-B	1.35E-02	3.38E-04	4.16E-08	2.85E-09	1.94E-07	5.36E-08	1.04	2.3	11.5	11.6	0.0021	2.8E-08
Twin Caves-A	1.43E-02	3.55E-04	4.40E-08	2.86E-09	2.13E-07	5.14E-07	0.20	1.9	Modern	Modern	0.0026	1.8E-07
Twin Caves-B	1.43E-02	3.55E-04	4.40E-08	2.86E-09	2.13E-07	5.14E-07	0.20	1.9	44.0	44.0	0.0026	2.8E-08
Gator Hole-A	1.39E-02	3.44E-04	4.37E-08	2.97E-09	2.07E-07	2.62E-06	0.15	0.7	Modern	2.6	0.0021	1.8E-07
Gator Hole-B	1.39E-02	3.44E-04	4.37E-08	2.97E-09	2.07E-07	2.62E-06	0.15	0.7	>55	>55	0.0021	2.8E-08
Heidi Hole-A	1.41E-02	3.51E-04	4.51E-08	2.76E-09	2.03E-07	5.38E-07	0.21	2.1	Modern	Modern	0.0066	1.8E-07
Heidi Hole-B	1.41E-02	3.51E-04	4.51E-08	2.76E-09	2.03E-07	5.38E-07	0.21	2.1	46.3	46.4	0.0066	2.8E-08
Hole in the Wall-A	1.36E-02	3.34E-04	4.30E-08	2.71E-09	1.96E-07	1.62E-07	0.44	1.9	15.4	15.5	0.0024	1.8E-07
Hole in the Wall-B	1.36E-02	3.34E-04	4.30E-08	2.71E-09	1.96E-07	1.62E-07	0.44	1.9	31.4	31.5	0.0024	2.8E-08

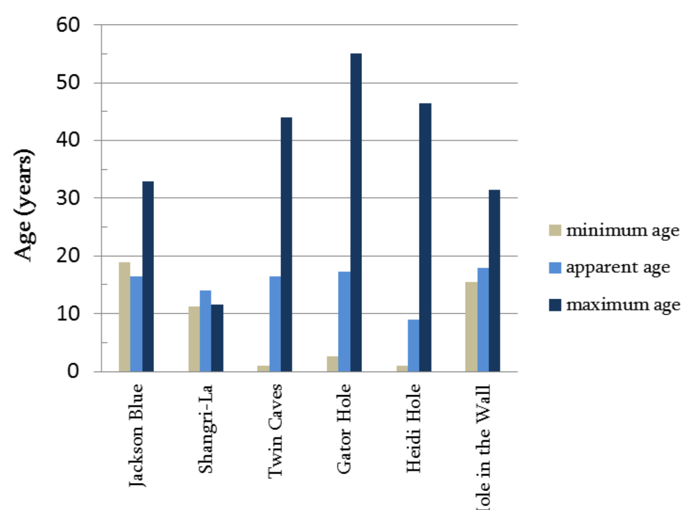
Sulfur Hexafluoride (SF_6) is another anthropogenic tracer that can be used to date ground water. SF_6 began to be produced industrially in 1953 for use in electrical switches and has rapidly increased in the atmosphere. The analysis of SF_6 concentration in ground water has been used successfully to date sand aquifers and karstic springs near the top of the Blue Ridge Mountains of Virginia (Plummer 1998). It is applicable to other environments, except where significant sources of natural, igneous SF_6 are found and complicate dating. Two factors can steer these ages either younger or older. One, if the samples have been diluted by mixing with old (SF_6 blank) water, the calculated apparent ages can be biased too old. Two, if the samples have mixed with water containing terrigenic SF_6, the apparent ages are biased too young. Since there are no large excesses of terrigenic SF_6 in the samples and other estimates of ground water age indicate a balance towards recent recharge, the results generated from this study (**Table 10**) indicate that SF_6 is the most reliable of the methods attempted to determine average recharge age. The calculated apparent (piston flow) ages range from about 9 to 18 years.

Table 10. Sulfur Hexafluoride (SF_6) Analysis Results

Sample Name	Sampling Date	Time	NOAA Scale fMol/L	Excess Air (mL)	SF6 fg/kg	Calculated SF6 (pptv) partial pressure	Piston flow model SF6 recharge year	Piston flow model SF6 recharge age
Jackson Blue-A	07/07/08	12:49	0.9174	1.0	133.99	2.82	1992.0	16.5
Jackson Blue-B	07/07/08	12:53	0.9343	1.0	136.46	2.87	1992.0	16.5
Shangri-La-A	07/08/08	10:15	0.9023	1.0	131.79	3.49	1995.0	13.5
Shangri-La-B	07/08/08	10:18	0.9113	1.0	133.09	3.27	1994.0	14.5
Twin Caves-A	07/08/08	13:13	0.9389	1.4	137.13	2.80	1992.0	16.5
Twin Caves-B	07/08/08	13:17	0.9016	1.4	131.69	2.83	1992.0	16.5
Gator Hole-A	07/09/08	14:42	1.3443	0.8	196.34	2.76	1991.5	17.0
Gator Hole-B	07/09/08	14:45	1.4363	0.8	209.77	2.65	1991.0	17.5
Heidi Hole-A	07/09/08	11:01	1.0966	0.8	160.15	4.38	1999.0	9.5
Heidi Hole-B	07/09/08	11:05	1.0273	0.8	150.04	4.68	2000.0	8.5
Hole in the Wall-A	07/08/08	16:49	0.7529	0.8	109.96	2.48	1990.5	18.0
Hole in the Wall-B	07/08/08	16:53	0.7682	0.8	112.20	2.53	1990.5	18.0

Table 11. Age Analysis Summary

Spring	Min age using ^3H EA (yr)	Max age using ^3H EA (yr)	Apparent Age using SF_6 (yr)
Jackson Blue	18.9	32.9	16.5
Shangri-La	11.2	11.6	14.0
Twin Caves	1.0	44.0	16.5
Gator Hole	2.6	55.0	17.3
Heidi Hole	1.0	46.4	9.0
Hole in the Wall	15.5	31.5	18.0



When the SF_6 results are combined the with tritium and tritium/helium-3 data, a clearer picture resolves regarding mixing and age (**Table 11**). The evidence supporting a mixing ratio weighted towards younger water from the tritium analysis is verified by the SF_6 results. The discharge from the springs of Merritt's Mill Pond consist of a mixture of very young to (relatively) old waters , favoring an apparent age of approximately 9-18 years. Compared to other springs studies in the state conducted by the USGS, SJRWMD, and SWFWMD, these ages are relatively young.

Stable Isotopes of Nitrogen

The nitrogen component of nitrate in ground water is composed of two stable isotopes, ^{14}N and ^{15}N, of which the vast majority of naturally occurring elemental nitrogen is ^{14}N. The difference between the two isotopes involves an extra neutron present in the nucleus of the ^{15}N isotope. The ratio of the two isotopes in the atmosphere is very constant; however, the additional weight conveyed by the presence of the neutron in N^{15} causes isotope fractionation in natural systems. Due to its lighter weight, ^{14}N is preferentially returned to the atmosphere during denitrification. Because animal and plant tissue will be ^{15}N enriched, nitrogen in ground water can be traced to an organic or inorganic source. Typically, nitrate in ground water with an enrichment of over 10 parts per thousand (⁰/₀₀) ^{15}N is considered representative of septic tank discharge and animal waste. Levels below 3 ⁰/₀₀ ^{15}N are representative of sources of nitrogen not entrained in the natural system such as inorganic fertilizer. Levels between 3 and 10 ⁰/₀₀ indicate mixed inorganic and organic sources (Katz et al 1998).

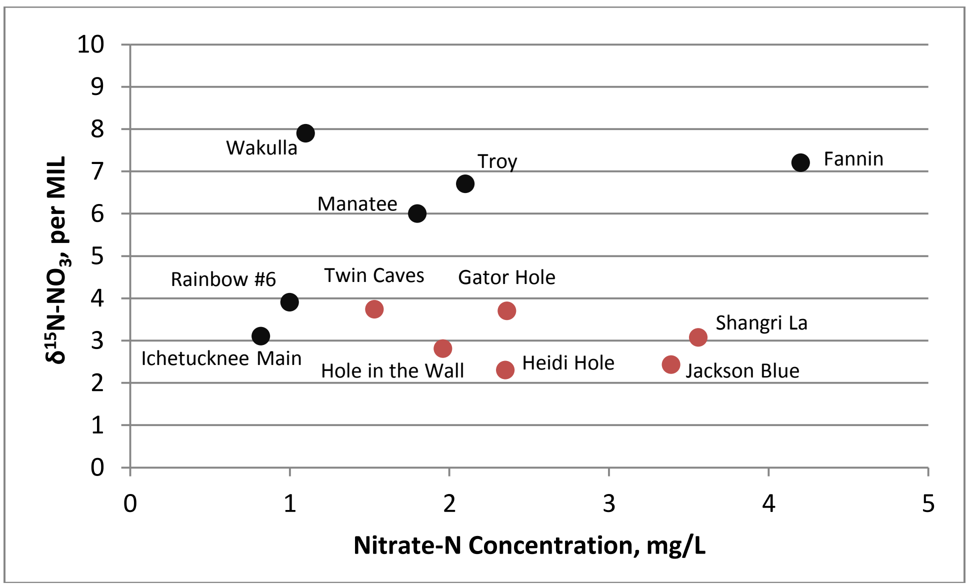


Figure 16. Nitrate-N Concentration vs. Delta ^{15}N

Sources of Nitrogen in Spring Water

The stable isotope results for the six springs sampled in Merritt's Mill Pond are presented in **Table 7**. The ^{15}N levels for all springs fall within or close to the range for inorganic sources of nitrogen and agree closely to the previously measured value for Jackson Blue Spring (Katz 2004). However, when charted against Nitrate-N concentration as in **Figure 16**, the springs separate into two groups. One group is composed of Jackson Blue and Shangri-La Springs, both with high Nitrate values and a relatively low ^{15}N ratio. The other four springs sampled fall into the second group with lower Nitrate values, two (Twin Caves and Gator Hole) with higher ^{15}N ratios indicating a more mixed nitrogen source. The second group of springs also has significantly higher concentrations of Kjeldahl Nitrogen (TKN) and the two with lower ^{15}N ratios have relatively elevated Ammonia concentrations. Concentrations of chloride and potassium correspond to elevated levels of nitrate, further supporting the fertilizer origin of nutrient contamination in ground water within and surrounding the Blue Spring springshed (Barrios and DeFosset 2005). The ratio of Delta ^{15}N to Delta ^{18}O also serves as an indicator of nitrogen sources, **Figure 17**. Low Delta ^{18}O levels in combination with lower Delta ^{15}N are attributable to an ammonia-based fertilizer source (Wassener 1995).

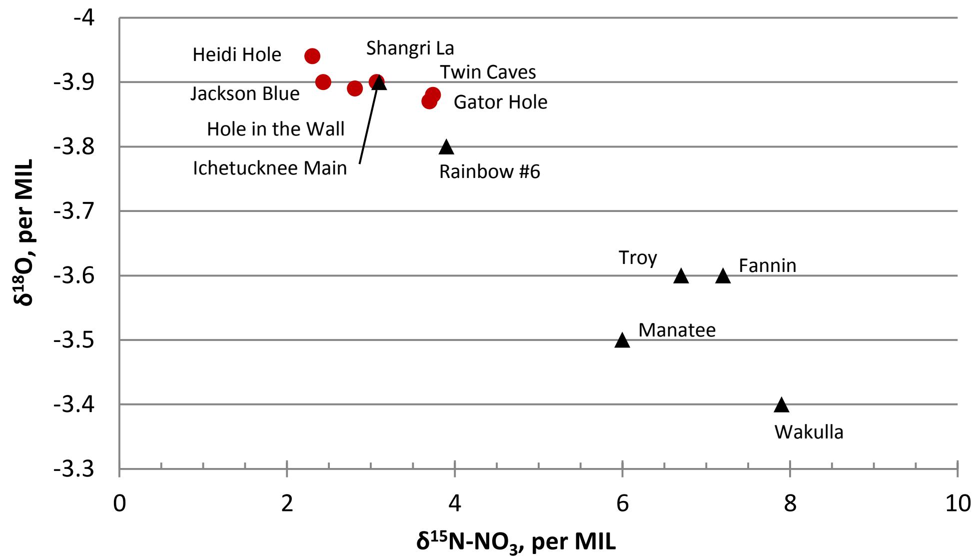


Figure 17. Delta ^{15}N vs. Delta ^{18}O

Estimation of Nitrogen Sources in Jackson County

The USDA Agricultural Census conducted every five years serves as an excellent source of data for land use on a county level. Since the District has discharge data from Jackson Blue Spring beginning in late 2004, for the purposes of this study, the year 2007 was used for estimating Nitrogen input loads from fertilizers, atmospheric deposition, animal waste, and septic tank effluent. The spring basin for Jackson Blue Spring is approximately 17% in area of the entire county. With the exception of livestock totals, which are based on the number of operations located within the springshed, it is assumed that county-wide statistics will apply proportionally to the spring basin.

In 2007, fertilizer sales of 3400 tons equivalent Nitrogen (N) were reported by the Florida Department of Agriculture and Consumer Services (DACS); and of this, 572 tons is estimated to have been applied to fields in the Jackson Blue Spring basin. Alternatively, the recommended application rate for crops published by the University of Florida Institute of Food and Agricultural Science can be used in combination with the National Agricultural Statistics Survey (NASS) and Census information for crops under tillage to produce a nitrogen application rate calculation of 442 tons N. For the creation of the nitrogen budget, the figure of 442 tons N is used since Nitrogen sales do not necessarily translate into local ground application. The 2007 report of the Jackson County livestock population in the Agricultural Census is summarized in **Table 12**. Estimates of nitrogen generated by animal waste are provided by the American Society of Agricultural Engineers (2005).

Table 12. Livestock Nitrogen Contribution in Jackson Blue Spring Basin, 2007

animals	Jackson County Head Count	lbs-N/head/day	lbs-N/head/year	lbs-N/year	tons-N/year	Jackson Blue Spring tons-N
cattle	54021	0.44	160.6	8675773	4338	174
chicken (layers)	6093	0.0035	1.3	7784	4	1
horses/ponies	2221	0.2	73.0	162133	81	14
goats	1573	0.06	21.9	34449	17	3

Domestic septic tank effluent inputs were estimated by multiplying the average N loading of 9 lbs per person per year (Otis et al 1993) and by the estimated population of 7236 (134 mi^2 x 54 hs/mi^2) living within the Jackson Blue springshed (US Census Bureau 2010). The resulting annual load is approximately 33 tons N/year. Atmospheric deposition concentration of 0.23 mg/L is based on measurements of nitrate and ammonium in rainfall collected at the NADP station in Gadsden County, FL in 2007. Due to drought, the annual rainfall accumulation of 2007 was very low at an average of approximately 38 inches for the basin leading to an annual atmospheric loading of 28 tons. Taking all of the inputs into account, the following chart, **Figure 18**, summarizes the nitrogen budget in 2007 for the Jackson Blue Spring basin.

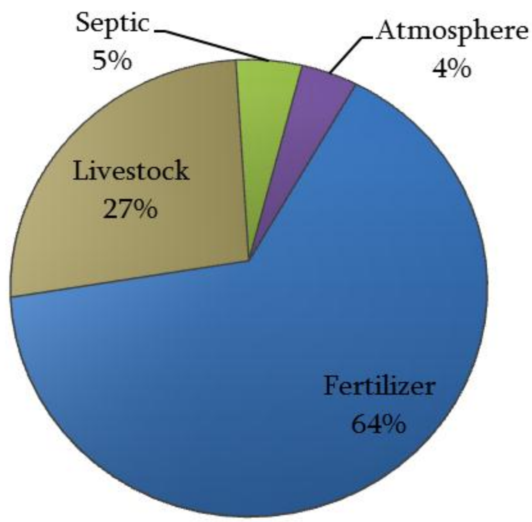


Figure 18. Nitrogen Application at Land Surface by Percent in 2007.

The stable nitrogen isotope results for Jackson Blue Spring clearly indicate an inorganic source. Given that the Jackson Blue Spring discharge has such as strong inorganic signature pointing to a fertilizer source for nitrogen, the source components of the discharge nitrogen are not proportional to the nitrogen land application. The estimated nitrogen inputs for fertilizer, livestock, and septic effluent do not account for losses of nitrogen through ammonia volatilization from fertilizer or the waste management of any given farm. Variations in manure management practices can lead to a range of nitrogen contribution to ground water between 6 and 60 percent of the total waste nitrogen. Since the rangeland in the spring basin is principally open forage land, animal waste is not concentrated in open disposal lots but rather distributed with the forage cover continuously over the course of the year. As a result, it can be concluded that nitrogen from livestock is somewhat conservative in the basin; either due to uptake by ground cover in pasture land or because the nutrients are being cycled effectively.

The annual loading of Nitrogen from Jackson Blue Spring for 2007 was 177 tons, calculated from the average concentration of 3.29 mg/L NO_3-N for the year multiplied by the average annual discharge of 54.8 cfs from the spring.

$$\text{Annual Load} = 3.29\ \text{mg/L} \times 28.31685\ \text{L/cf} \times 1.0 \times 10^{-6}\ \text{kg/mg} \times 1.72 \times 10^{9}\ \text{cf/year} \times 0.001102\ \text{tons/kg} = 177\ \text{tons N}$$

As shown in **Figure 19**, there has been a substantial reduction in total acres under tillage for field crops following a peak in the 1970s. However, the NO_3-N concentration measured at Jackson Blue Spring has continued to rise (**Figure 10**). The reduction in agricultural acres under tillage occurred predominantly at the expense of soybeans; which, like peanuts, are a nitrogen-fixing legume crop and require minimal fertilization. Furthermore, the decrease in corn acreage has been offset by the increase of cotton cultivation.

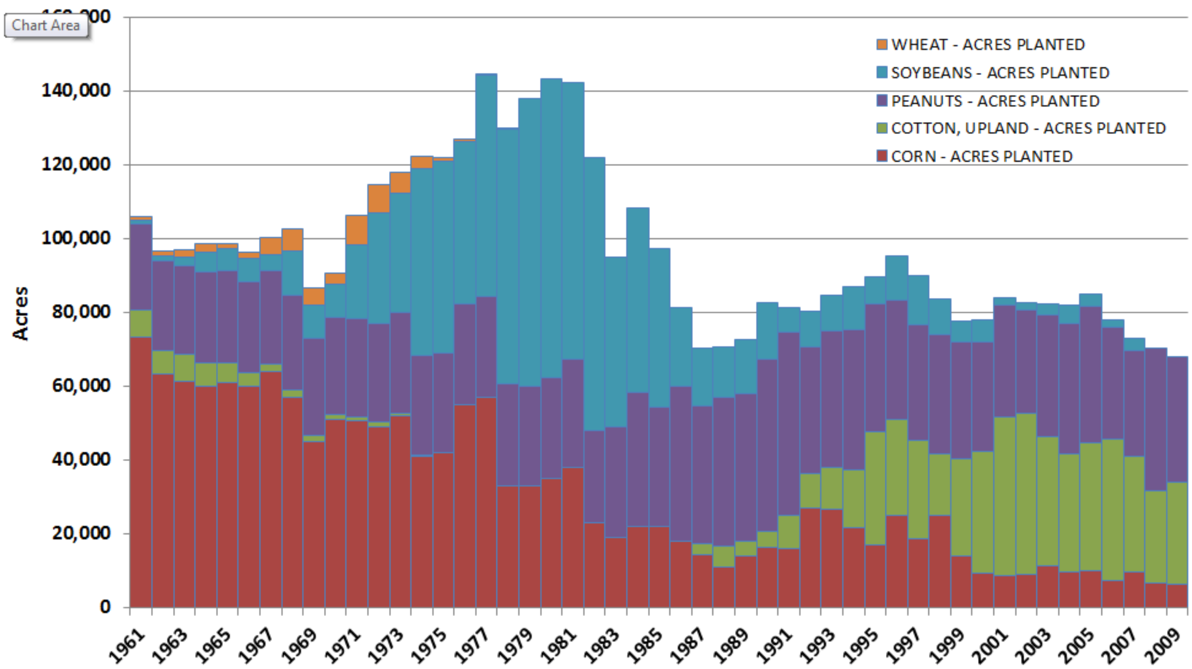


Figure 19. Field Crops – Jackson County Reported Acres in Cultivation

Table 13. 2007 NASS Census - Acres Under Tillage and Nitrogen Loading Estimate

crops	acres	N lbs/acre	Jackson Blue Spring Acres	Estimated Fertilizer Application	
				lbs	tons
cotton	31200	60	5241.6	314496	157
peanuts	32743	0	5500.8	0	0
forage	20116	100	3379.5	337949	169
corn-grain	4886	125	820.8	102606	51
vegetables	3883	200	652.3	130469	65

The 2007 NASS Census results indicate corn and cotton comprise roughly 50 percent of the agricultural fertilizer application rate estimated for the spring basin (**Table 13**). Sufficient NASS tillage data exist to calculate nitrogen fertilizer application for these two field crops from 1961 to present (**Figure 20**). Keeping in mind that the totals presented do not represent additional loads from forage crops, vegetables, or other applications, the exact composite nitrogen application over that time period is difficult to calculate accurately. Carrying the assumption that forage and vegetable nitrogen fertilizer application remains near 50 percent for the spring basin as calculated for 2007, it is possible to create a reasonable history of nitrogen loading to the aquifer over that time. The maximum age for Jackson Blue Spring discharge of approximately 33 years combined with an apparent age of approximately 17 years means that the current nitrate discharge is a result of fertilizer application conducted since the late-1970s and weighted to application conducted in 1994.

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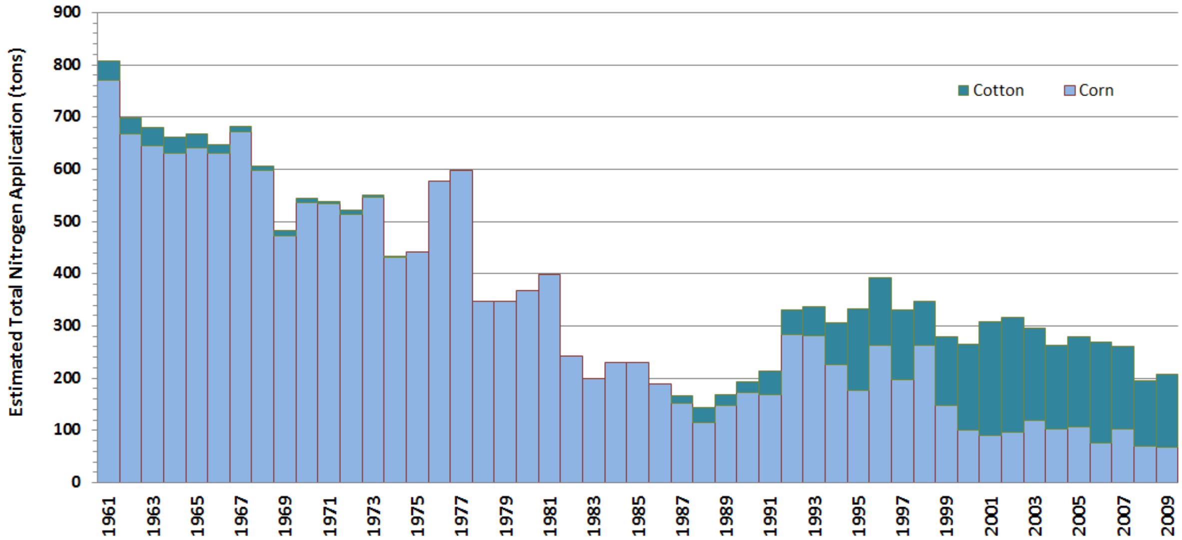

Figure 20. Estimated Corn and Cotton Fertilizer Application (from 1961-2009 NASS Survey cultivation)

The average annual nitrogen fertilizer application total for the 33-year period from 1976 to 2009 is approximately 600 tons compared to the average annual discharge loading of approximately 350 tons, resulting in successful uptake of approximately 250 tons/year (42-percent efficiency). Under any condition, it is easy to conclude that nitrogen fertilizer in the basin is not conservative and that a substantial proportion is discharging from Jackson Blue Spring and the other springs in Merritt's Mill Pond. As long as the total nitrogen loading from surface application exceeds the discharge loading from Jackson Blue Spring, nitrate concentration in storage should increase. The results of subtracting the discharge loading calculated from measured and interpolated nitrate concentrations to 1961 and backcasted discharge for Jackson Blue Spring (based on the USGS Altha gauge, Barrios et al 2011) from the thirty-three year rolling average of estimated nitrogen fertilizer application are presented in **Figure 21,** with the load in storage peaking between 1990 to 1992.

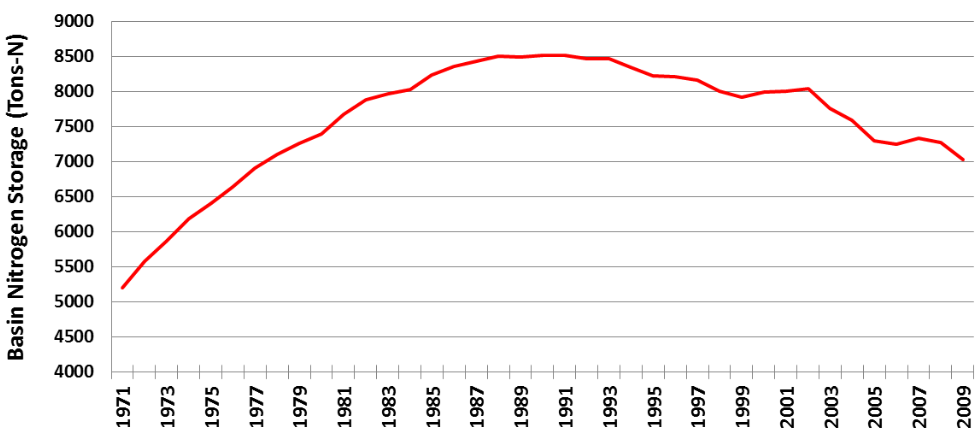

Figure 21. Jackson Blue Spring Basin Fertilizer-Based Nitrogen Storage

Changes in the types of crops in cultivation reducing the fertilizer loading rate combined with increasing nitrate discharge from Jackson Blue Spring flattened and then reversed the rate of nitrogen storage beginning in the early 1990's; this is reflected in the relatively slow increase in nitrate concentration in Jackson Blue Spring over the course of the past decade. Once the seventeen-year average period of spring discharge passes the peak nitrate storage level, the nitrate concentration in Jackson Blue Spring should slowly decline. The lower nitrate concentrations measured in 2010-2011 following the peak results from 2008-2009 seem to verify this hypothesis.

A statistical model of nitrate response base on nitrogen storage, fertilizer application, and spring discharge was created to estimate changes in nitrate concentration from Jackson Blue Spring under several fertilizer use scenarios from 2011 through 2050; the results of which are presented in **Figure 22**. The estimates are based on key assumptions: 1) Jackson Blue Spring discharge remains near the long term average of approximately 113 cfs and 2) all sources of nitrogen loading remain constant with the exception of fertilizer application.

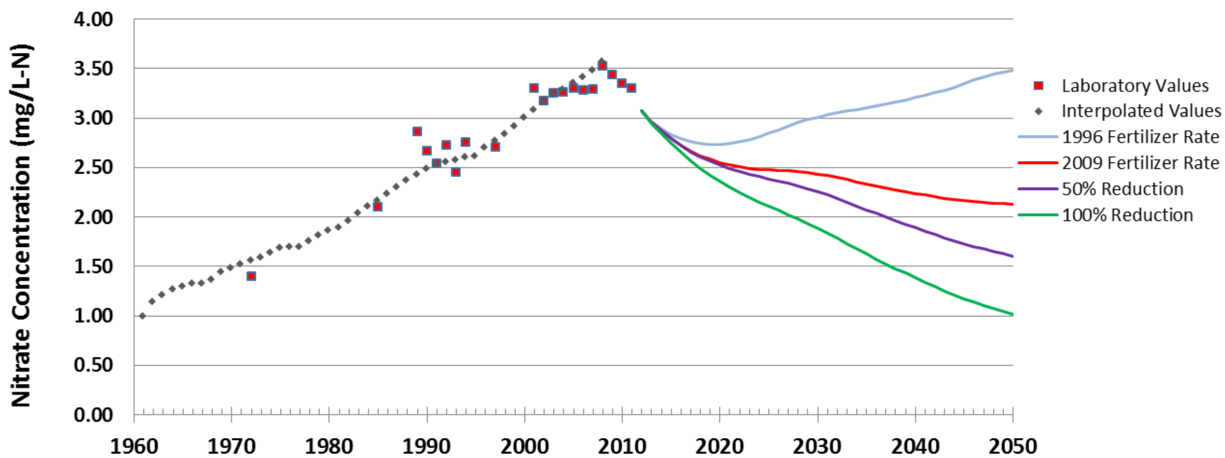

Figure 22. Model of Nitrate Concentration Response to Changes in Fertilizer Application

Given the uncertainty of the variables used in the predictive model, it serves best as a framework for understanding the response of the system to changes in landuse and hydrologic conditions. For instance, drought conditions, as observed during most of 2011, cause several problems in predicting nitrate concentration. Lower discharge curtails the ability of the system to remove nitrate from storage. Also, lower recharge reduces the amount of lower nitrate ground water displacing water recharged during heavier fertilizer application periods. Under the scenarios presented, if fertilizer application continues at 2009 rates, nitrate concentration at Jackson Blue Spring decreases and stabilizes near 2 mg/L approaching 2050. A 50% reduction in fertilizer application over the next 10 years results in a further reduction of 0.5 mg/L to 1.5 mg/L in concentration by 2050. If fertilizer application were to halt completely after 2010, nitrate concentration would drop to approximately 1.0 mg/L by 2050. A final scenario returns fertilizer application rates to 1996 levels, when more land was reported under cultivation and a higher percentage of that land was dedicated to more fertilizer-dependent corn cultivation. Under this last condition, nitrate concentration decreases for a decade, begins to increase again, and then stabilizes near 3.5 mg/L by 2050.

Summary and Conclusions

At least eight springs are located within Merritt's Mill Pond. Six of those were determined to have measurable discharge during the study period. Jackson Blue Spring, classified a first magnitude, was measured at discharges of less than 100 cfs several times during the course of the study. A significant correlation between ground water elevation in the spring basin and Jackson Blue Spring discharge was found in the Pittman/VISA well located in Two Egg. The District used this correlation and that with base flow calculations of the Chipola River to construct a long-term discharge record for Jackson Blue Spring. The District also collected discharge measurements from the minor spring vents in the Mill Pond – with the springs ranging from third to fourth magnitude. However, the submerged measurements were conducted during the height of the 2006-2007 drought and likely reflect low flow conditions.

The combined use of instrument survey and LiDAR allows a high resolution view of the Floridan Aquifer potentiometric surface, providing a better understanding of flow directions and spring catchments in Northeast Jackson County. The spring basin delineated from the potentiometric surface extends over an area with few surface water expressions. The basin size of 133 square miles agrees with an average estimated recharge rate of 12-16 inches for the karst area and mean ground water discharge of 113 cfs for Jackson Blue Spring.

Individual differences in water quality results indicate that the springs have discreet contribution areas influenced by local geology and land use. However, the six springs of Merritt's Mill Pond sampled for this project can be divided into two groups. The first group, comprising Jackson Blue and Shangri-La springs, has a signature identifying a ground water source originating in the Eocene Ocala Formation and residuum to the north and east. The second group, comprising Twin Caves, Heidi Hole, and Hole-in-the-Wall springs, has a signature associated with the Miocene Marianna/Suwannee Limestone to the south and west. Nitrate concentrations have increased substantially in Jackson Blue Spring over the past 50 years. The other springs sampled for the project also show high nitrate concentrations.

The comparison of land use from 1994 to 2004 indicated a decrease in forested land with a corresponding increase in built-up land and agricultural land. A modest correlation between water quality and land use exists between agricultural land and forest land with agricultural land exhibiting a higher impact on water quality.

The age of ground water discharging from the springs measured for the project are best determined by a combination of SF_6 and Tritium/Helium data. The apparent ages of all springs fell within a relatively young range of 9-18 years, with tritium data providing estimates of minimum and maximum ages between modern and approximately 55 years. The four southern springs have the greatest range of recharge age and likely have large contributions of very young water with a minor component of very old water. Jackson Blue and Shangri-La seem to be discharge points for water moving quickly over a large area that is well integrated. The downstream springs seem to be discharging very old water captured from lower in the regional flow path and very young water recharged in close proximity.

Stable nitrogen isotope data was collected from six springs for the project. All results indicated a nitrogen source of inorganic nature and point to fertilizer as the cause of the elevated nitrate levels. Two springs, Gator Hole and Twin Caves show indications of slightly more wastewater contribution. Chloride concentrations are also elevated in springs in close proximity to residential developments, indicating increased wastewater influence not measureable against the overwhelming fertilizer signature in the basin. Concentrations of dissolved gases are consistent with atmospheric equilibration during ground water recharge and indicate that denitrification has not removed significant amounts of nitrate from the system. Therefore, the gas results confirm that the stable nitrogen isotope results accurately describe the sources of nitrogen.

Historic agricultural cultivation data coupled with recommended fertilizer application rates correlate well with observed nitrate concentration measured at Jackson Blue Spring after adjusting for discharge age and ground water residence time. A predictive model of Jackson Blue Spring nitrate indicates that concentration should have peaked around 2008-2009 followed by a gradual reduction in concentration. Results from 2010-2011 nitrate analysis seem to verify the model prediction, however, continued monitoring of water quality and discharge from Jackson Blue Spring should remain a priority.

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