TEMPORAL WATER CHEMISTRY TRENDS WITHIN INDIVIDUAL SPRINGS AND WITHIN A POPULATION OF FLORIDA SPRINGS

By

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Florida's springs provide a way to assess groundwater quality because their discharge integrates (spatially and temporally) groundwater from large parts of the aquifer. Nutrient enrichment of Florida's springs, specifically by nitrate and phosphorus, is a major issue in the 21st century due to the concerns over "blue-baby" syndrome and the potential eutrophication of their receiving waters, i.e., spring runs, rivers, and estuaries. I assessed whether temporal changes (1907-2003) in water chemistries had occurred in 109 springs, with an emphasis on total phosphorus and nitrate-nitrogen.

As a group, Florida springs exhibit a wide range of water chemistries. However, the springs, in general, can be characterized as alkaline (pH averaging 7.4) and chemically-rich (specific conductance averaging 713 μS/cm @ 25 C). Total alkalinity and total hardness values average 137 and 244 mg/L as $CaCO_3$, respectively; thus the springs are considered to be hardwater. The waters are also nutrient-rich with total phosphorus concentration averaging 0.054 mg/L and total nitrogen concentration averaging 1.6 mg/L.

Individual spring analyses were conducted by regressing analytes with year. In these within-spring analyses, there were significant ($p<0.05$) temporal changes within individual springs over time in pH (2 increases, 12 decreases), total specific conductivity (26 increases, 1 decrease), total alkalinity (2 increases, 0 decreases), chloride (9 increases, 5 decreases), total hardness (6 increases, 1 decrease), total phosphorus (1 increase, 1 decrease), and nitrate-nitrogen (17 increases, 1 decrease). There were no statistically significant changes in orthophosphate concentrations within any of the springs. Time period comparisons within the population (paired *t*-tests) were conducted for each analyte (3 comparisons per analyte) by comparing three time periods designated as early (1907-1979), middle (1980-1989), and recent (1990-2003). Data before 1977 were accepted as baseline data for the springs and were used to construct the early time period data set. The middle time period data were mostly from a single study of 35 springs in 1985. The recent time period was developed because of the perceived idea that these data are the result of the best quality assurance quality control methods available. There was a statistically significant ($p<0.05$) decrease in median pH, and increases in mean values of total specific conductivity, total alkalinity, total hardness, and nitrate-nitrogen in eight of the 24 time period comparisons. Mean concentrations of chloride, total phosphorus, and orthophosphate did not exhibit significant changes in any of the time period comparisons. There was a significant increase in mean nitrate-nitrogen concentration in the early versus middle (0.39 mg/L and 0.71 mg/L, respectively) and early versus recent (0.46 mg/L and 1.04 mg/L, respectively) time period comparisons.

CHAPTER 1
INTRODUCTION

Florida's springs are an invaluable natural resource to fish, wildlife and the citizens and visitors of Florida. They also provide a way to assess groundwater quality because their discharge integrates (spatially and temporally) groundwater from large parts of the aquifer (Katz et al. 1999). The Floridan aquifer (the water source for many springs) supplies most of the state's drinking water, as well as water for agriculture and other industries.

The population of Florida has increased from 6.7 million people in 1970 to 16.7 million in 2002 (US Bureau of the Census 2002). Increased anthropogenic activities, like development and water use, can cause changes in spring water chemistry and spring flow (Jones et al. 1996; Champion and Starks 2001). Nutrient enrichment of Florida's springs, specifically by nitrate and phosphorus, is a major issue due to the concerns over "blue baby" syndrome and the potential eutrophication of their receiving waters; i.e., spring runs, rivers, and estuaries (Jones et al. 1994; Jones et al. 1996; Champion and Starks 2001).

In 1947, the Florida Geological Survey (FGS) published the first Springs of Florida Bulletin No. 31, which provided water chemistry data on some of the more popular and important springs in the state (Ferguson et al. 1947). In 1977, a revised version of this bulletin, encompassing over 200 Florida springs, was published (Rosenau et al. 1977), which included data on previously undescribed springs. Much of these data have been accepted as baseline water chemistry data for the springs.

In recent years, there has been increased water chemistry monitoring of springs across the state due to the concerns over “blue baby” syndrome, eutrophication, and degraded groundwater quality. The water management districts of Florida, the Florida Department of Environmental Protection, Florida Geological Survey, and the United States Geological Survey have published many reports on spring water chemistries suggesting nutrients, especially nitrate concentrations, have been increasing (Jones and Upchurch 1993; Hornsby and Mattson 1998; Katz et al. 1999; Champion and DeWitt 2000).

Nitrate is one of the chemical compounds for which there is a State of Florida water quality standard or guideline (Florida Administrative Code 62-550). Nitrate is subject to Florida’s primary drinking water standard of 10 mg/L as N or 44 mg/L as NO_3^- (Florida Department of Environmental Regulation 1989). A major cause for concern when dealing with nitrate is methemoglobinemia, an excess of methemoglobin, which causes oxygen deprivation. Infants and young children are especially susceptible to this condition, which may result in “blue baby” syndrome (Hem 1986).

Increases in nitrate-nitrogen concentration, nitrogen being an essential nutrient for plants, have been reported in many Florida springs in the Suwannee River Basin (Katz et al. 1999) and along the west coast of Florida (Jones et al. 1996; Champion and DeWitt 2000; Champion and Starks 2001). Nutrients in groundwater discharging from springs have been thought to contribute to increased macrophyte and algal biomass downstream and in areas of submarine springs, such as bays in Florida (Jones et al. 1994; Jones et al. 1996). Dense growths of submersed vegetation, especially hydrilla (*Hydrilla verticillata*) and lyngbya (*Lyngbya* sp.) have restricted navigation and recreational uses in effected areas (Jones et al. 1994; Jones et al. 1996, Terrell and Canfield 1996). There is also a section of the Florida Administrative Code (FAC) that addresses the eutrophication of water bodies. This section states that "in no case shall nutrient concentrations of a body of water be altered so as to cause an imbalance in natural populations of aquatic flora or fauna" (FAC 302.300, 62-302.700, 62-4.242)

To mitigate adverse effects on water quality flowing from the springs of Florida, some government agencies are communicating with and advising industries and agriculture that could be or are contributing to the nutrient enrichment of groundwater. For example, the Suwannee River Water Management District is working with local farmers to implement best management plans, while the Florida Spring's Task Force develops strategies for the protection and restoration of Florida's springs.

To characterize water chemistries in springs, studies have been conducted by the aforementioned agencies and some universities. Some of these efforts have documented short-term water chemistry changes in individual springs and spring complexes (e.g., Jones et al. 1996; Champion and DeWitt 2000; Champion and Starks 2001). There, however, are no studies that have used long-term water chemistry data from a large number of Florida springs to test if significant changes in water chemistry have occurred within individual springs or within the population of Florida springs.

My objectives, therefore, were to evaluate potential changes (e.g., temporal trends) in water chemistry within individual springs and within a population of Florida springs using available long-term data. Particular attention was given to total phosphorus and nitrate-nitrogen concentrations because phosphorus and nitrogen are often considered to be the primary limiting plant nutrients when eutrophication concerns arise, and elevated nitrate concentrations are of concern with respect to “blue baby” syndrome.

CHAPTER 2
METHODS

Nearly 600 springs are known to exist in Florida (Florida Springs Task Force 2000). Springs are separated into eight classifications based upon the volume of water they produce each day. Spring water discharge is dependent on many factors, such as the size of the recharge basin, the hydraulic gradient, and the amount of rainfall that the recharge area receives (Katz et al. 1999). The largest are classified as 1^{st} magnitude springs, of which there are 33 known to exist in Florida, each producing at least 2.83 m^3 per second (64 million gallons of water per day). In this study, water chemistry data were obtained from 25 1^{st} magnitude springs ($\geq$ 2.83 m^3/s), 59 2^{nd} magnitude springs (0.2832 m^3/s to 2.82 m^3/s), and 25 3^{rd} or lower magnitude springs (<0.2832 m^3/s).

Field and Laboratory Procedures

I began collecting surface water samples from the spring boils (springs studied by Rosenau et al. 1977) in the summer of 2003 for analyses of pH, total specific conductivity, total alkalinity, total chloride, total hardness, total phosphorus, total nitrogen, and total nitrate-nitrogen. Surface water samples from 40 springs across the state were collected once between July 2003 and December 2003. The majority of the sampled springs were 2^{nd} magnitude springs and lower (<2.83 m^3/s), due to the large amount of available data for 1^{st} magnitude springs (e.g., Jones et al. 1994; Jones et al. 1996; Scott et al. 2002). Water samples were collected in triplicate from just below the surface (ca. 0.5 m) using 1-L acid-washed, triple-rinsed brown Nalgene bottles. Samples were placed on ice and transported within 24 hours to the Department of Fisheries and Aquatic Sciences water chemistry laboratory at the University of Florida for analysis.

An Accument model 10 pH meter calibrated with buffers of pH 4.0 and 7.0 was used to measure pH. Specific conductance (μS/cm @ 25°C) was measured using a Yellow Springs Instrument Model 35 conductance meter. Total alkalinity concentrations (mg/L as $CaCO_3$) were determined by titration with 0.02 N sulfuric acid (Method 2320 B; APHA 1992). Chloride concentrations (mg/L) were determined by titration with 0.0141 N mercuric nitrate. Diphenylcarbazone reagent was used for endpoint determination (Adapted from Method 4500 Cl^- C; APHA 1992). Total hardness concentrations (mg/L as $CaCO_3$) were determined by EDTA titration (Method 2340 C; APHA 1998), which was modified using HACH chemicals. Total phosphorus concentrations (mg/L) were determined using the procedures of Murphy and Riley (1962), with a persulfate digestion (Menzel and Corwin 1965). Total nitrogen concentrations (mg/L) were determined by oxidizing water samples with persulfate and determining nitrate-nitrogen concentration with second derivative spectroscopy (D’Elia et al. 1977; Simal et al. 1985; Wollin 1987). Nitrate-nitrogen concentrations (mg/L as N) were determined using an automated cadmium reduction method (4500-NO3-F; APHA 1998).

The results of my water chemistry analyses were combined with agency data from springs to obtain water chemistries for a total of 109 springs, with sampling dates ranging from 1907 to 2003. I also included orthophosphate data from the agency spring water chemistries because of its abundance in the past and recent spring data. For the within-population analyses I divided the data into three sampling periods: early (1907-1979), middle (1980-1989), and recent (1990-2003). Data from Rosenau et al. (1977) were used to develop the early time period because these data were accepted to be the baseline data for the springs. The middle time period data were mostly from a single study on 35 springs in 1985. The recent time period was developed because of the perceived idea that these data are the result of the best quality assurance quality control methods available.

Rosenau et al. (1977) cites Rainwater and Thatcher (1960) for all methods of water collection before 1970, and Brown et al. (1970) for all collection and analysis between 1970 and 1977. Water sampling and analyses by other agencies complied with the procedures set forth by the United States Environmental Protection Agency, the American Public Health Association, the United States Geological Survey, and others. The Florida Department of Environmental Protection used their Standard Operating Procedures (Florida Department of Environmental Protection 2002).

Statistical Analyses

Data from the triplicate water samples, that I collected from each spring, were averaged (except pH) to obtain a single arithmetic mean for the springs analyses. Median values for pH were used rather than mean values.

Individual springs were analyzed by plotting each analyte concentration against time. Only springs, that contained data from before and after 1990, were analyzed. Linear regression analyses were used to determine whether a springs' water chemistry had changed.

Nutrient concentrations can have profound effects on aquatic ecosystems. Thus, I analyzed temporal variation in some of the more studied nutrients (total phosphorus and nitrate-nitrogen) in spring water. Recent time period (1990-2003) data were utilized to assess total phosphorus and nitrate-nitrogen variance in the springs. I used the recent time period because this time period contained the most data and because analytical methodologies have improved since the early and middle time periods. Springs in the recent time period that contained ≥ 10 sampling dates were used in this analysis. Defining normal temporal variation with respect to nutrient concentration in lakes is difficult because certain watershed activities, point source additions, water level manipulations and other activities can have significant impacts (Cooke et al. 1993). I felt these activities could impact spring chemistries as well. Therefore, the relation between year and total phosphorus and year and nitrate-nitrogen for each spring was individually examined.

Individual spring variance was calculated according to Knowlton et al. (1984):

$$s^2 = \Sigma\,(X_M - X_L)^2 * (m-1)^{-1} \qquad (1)$$

where X_M is the individual sample, X_L is the spring mean for all samples, and m is the number of samples.

To satisfy the homogeneity of variance assumption of parametric statistical analysis (Snedecor and Cochran 1979), the correlation between variances and means was removed by transforming data to base 10 logarithms, after adding 0.001 mg/L and 0.01 mg/L (detection limits) to the total phosphorus and nitrate-nitrogen data, respectively, prior to analysis. Because of the unfamiliar scale of variance estimates expressed in logarithmic units, the magnitude of the variances were described, as follows:

$$\%\ \text{variance} = 50[10^{\sqrt{a}} - 1/10^{\sqrt{a}}] \qquad (2)$$

where “a” is the value of s^2 from equation 1. These values express variance as a percent of the mean and are approximately equal to coefficients of variation calculated from untransformed data (Snedecor and Cochran 1979). The individual spring sample percent variances were then averaged to obtain a mean percent variance for each spring for total phosphorus and nitrate-nitrogen. All spring means were then averaged to calculate a grand mean, median and standard deviation for the population of springs.

To assess general temporal patterns within the population of springs, I used data from each of the following time periods: early (1907-1979), middle (1980-1989), and recent (1990-2003). To determine if there were any significant changes in water chemistry over the three time periods, a median value for pH, and mean values for total specific conductivity, total alkalinity, chloride, total hardness, total phosphorus, orthophosphate, and nitrate-nitrogen were calculated for each spring in each time period. Data between time periods were analyzed using paired *t* tests (SAS Institute, Inc. 1994) and also plotted on a 1:1 line for visual examination. Springs with analyte concentrations above or below the 95 percent confidence interval around the 1:1 line were considered to be outliers (extreme values). Outliers will be named throughout this study to indicate those springs that expressed characteristics in water chemistry that were statistically different from the rest of the population. Because of the lack of total nitrogen data before 1990, this analyte was excluded from both the individual and time period analyses. All data, except pH, were transformed to base 10 logarithms, after correcting for reported zero values, to accommodate heterogeneity of variances (Snedecor and Cochran 1979) for the time period comparisons.

Statements of statistical significance imply $p \leq 0.05$. All statistical analyses were performed using JMP (SAS Institute, Inc. 1994).

CHAPTER 3
RESULTS AND DISCUSSION

As a group, Florida springs are quite variable with respect to water chemistry (Table 1). However, using the recent time period data, the springs, in general, can be characterized as alkaline (pH averaging 7.4) and chemically-rich (specific conductance averaging 713 μS/cm @ 25 C). Total alkalinity and total hardness values averaged 137 mg/L as $CaCO_3$ and 244 mg/L as $CaCO_3$, respectively, thus the springs are considered to be hardwater. The waters are also nutrient-rich with total phosphorus concentration averaging 0.054 mg/L and total nitrogen concentration averaging 1.6 mg/L (Table 1). Consequently, some of the Florida springs are among some of the most biologically productive aquatic systems in the world (Odum 1957 a, b; Duarte and Canfield 1990).

General Chemistry Analytes

Within-Spring Analyses

In the within-spring analyses, statistically significant changes in water chemistry over time were detected for 48 springs. Many of the temporal changes detected, however, I considered to be questionable. For example, I thought that the significant decrease in pH (Figure 1) in Weeki Wachee Spring (Hernando Co.) was confounded because of the low number of samples before 1990 compared to the relatively large number of samples after 1990. I did, however, consider that 12 significant changes in spring water chemistries detected by regression analyses were important to consider. In Gainer #2 Spring (Bay Co.) pH increased from 7.3 to 8.2, while pH decreased in Lettuce Lake Spring (Hillsborough Co.) from 8.2 to 7.2. Specific conductivity (μS/cm @ 25 C) increased in Turtle (Lafayette Co.; 282 to 404), Homosassa (Citrus Co.; 2590 to 4486), Hart (Gilchrist Co.; 355 to 429), Branford (Suwannee Co.; 345 to 476) Gainer #2 (Bay Co.; 82 to 130), Fanning (Levy Co.; 357 to 478) (Figure 2), and Weeki Wachee (Hernando Co.; 262 to 302) Springs, while specific conductivity decreased in Beckton Spring (Washington Co.; 275 to 130). Chloride concentration increased in Tarpon Hole Spring (Citrus Co.; 180 mg/L to 540 mg/L), whereas total hardness increased in Homosassa Springs (Citrus Co.; 360 mg/L $CaCO_3$ to 612 mg/L $CaCO_3$).

Time Period Analyses

Early time period vs. middle time period

When considered as a population of springs, mean chemistries in each of the time periods displayed a wide range in concentration (Table 2). In the time period comparisons, there was a significant decrease in median pH from 7.6 in the early time period to 7.4 in the middle (Table 3, Figure 3). In Table 3, analyte values are sometimes different for the same time period depending on the comparison. For example, early pH in the early versus middle time period comparison is 7.7, but in the early versus recent time period comparison early pH is 7.6. These differences arise because the time period analyses did not utilize the same springs in each comparison.

Fanning (Levy Co.) and Hornsby (Alachua Co.) Springs were outside of the calculated 95^{th} percentile for pH. Median pH in these springs decreased from 8.0 to 6.6 and from 8.8 to 7.0, respectively. Outliers may arise because of an error in recording the data, error entering the data into a computer, because the data were obtained under different conditions than the rest of the observations (Ott and Longnecker 2001) or because relatively large changes occurred. Blue Spring (Levy Co.) was outside the calculated 95^{th} percentile for total specific conductivity (µS/cm @ 25°C). Mean specific conductance in this spring decreased from 363 to 216. Blue (Madison Co.) and Alexander (Lake Co.) Springs were outside the calculated 95th percentile for total alkalinity (mg/L as $CaCO_3$). Mean total alkalinity in these springs decreased from 120 to 61 and from 120 to 81, respectively. This time period comparison was not conducted for chloride or total hardness due to a lack of available data for the middle time period.

Early time period vs. recent time period. In the early versus recent time period comparisons, there was a significant decrease in median pH and significant increases in mean values of total specific conductivity, total alkalinity, and total hardness (Table 3; Figures 4, 5, 6, and 7). Median pH decreased from 7.6 to 7.4, while mean values for total specific conductivity (μS/cm @ 25°C), total alkalinity (mg/L as $CaCO_3$) and total hardness (mg/L as $CaCO_3$) increased from 610 to 730, 120 to 140, and from 190 to 240, respectively.

In this time period comparison, Carlton (Taylor Co.; 7.8 to 6.7), Hornsby (Alachua Co.; 8.8 to 7.3), Lettuce Lake (Hillsborough Co.; 8.2 to 7.1), and Indian (Wakulla Co.; 8.1 to 7.1) Springs were outside of the calculated 95th percentile for pH. Tarpon Hole (Citrus Co.; 555 to 2188), Boat (Hernando Co.; 282 to 843), Beckton (Washington Co.; 273 to 134), Carlton (Taylor Co.; 300 to 107), and Glen (Alachua Co.; 157 to 334) Springs were outside of the calculated 95th percentile for total specific conductivity.

A spring may become more vulnerable to salt-water influence the closer that spring is to coastal areas (Jones et al. 1994). As the salt-water/fresh-water transition zone moves toward and away from land, water quality characteristics, such as conductivity and chloride, in the springs change (Jones et al. 1994). Conductivity increases with increasing concentrations of salts, acids, and bases, where these concentrations are dependent on factors such as rainfall and catchment area size (Kalff 2002). Generally, larger catchments yield higher conductivities due to an increase in evapotranspiration time as well as longer contact of the runoff with rock and soil (Kalff 2002). For this study, four of the five springs that were outside of the calculated 95th percentile for total specific conductivity were in western coastal counties, which suggests a strong influence by the Gulf of Mexico.

Although the difference between mean chloride concentration in the early and the recent time periods was not statistically significant, there were three springs that were outside of the calculated 95th percentile. Mean chloride (mg/L) in Boat Springs (Hernando Co.) increased from 16.9 to 139, while mean chloride decreased in Beckton Spring (Washington Co.) and Siphon Creek Rise (Gilchrist Co.) from 21 to 0.67 and 1200 to 13, respectively. Boat Spring (Hernando Co.) water level is partially controlled by nearby Hammock Creek, which is tidally influenced (Rosenau et al. 1977). The change in chloride in Boat Spring may have resulted from sampling at different tides.

Health (Pinellas Co.), Beckton (Washington Co.) and Cypress (Washington Co.) Springs were outside the calculated 95th percentile for total alkalinity. Mean total alkalinity (mg/L as $CaCO_3$) in Health Spring increased from 84 to 191, while mean values in Beckton and Cypress Springs decreased from 110 to 45 and from 94 to 30, respectively. Health Spring (Pinellas Co.) was also outside the calculated 95th percentile for total hardness (mg/L $CaCO_3$). Mean total hardness in this spring increased from 90 to 430.

Middle time period vs. recent time period. In the middle versus recent time period comparisons, there was again a significant change in total specific conductivity (μS/cm @ 25°C), in which the mean value for the sample population of springs increased from 569 to 618 (Table 3; Figure 8). There were no outliers for conductivity, pH, or total alkalinity in this time period comparison. No comparisons were made for chloride or total hardness due to a lack of available data for the middle time period.

Nutrients

Phosphorus

Total phosphorus data from my spring water analyses in 2003 (N=40) yielded a mean concentration of 0.045 mg/L with a range of 0.005 mg/L to 0.313 mg/L. Comparatively, recent time period (1990-2003) agency total phosphorus data (N=89) yielded a mean of 0.053 mg/L with a range of 0.005 mg/L to 0.175 mg/L. These two independently collected data sets indicated similar mean values and that there is a wide range in total phosphorus concentration in spring waters.

Within-spring analyses

In the within-spring analyses, statistically significant changes in total phosphorus were detected in Telford (Suwannee Co.; 0.052 mg/L to 0.050 mg/L, N=55) and Wacissa #2 (Jefferson Co.; 0.02 mg/L to 0.04 mg/L, N=3) Springs. For Telford Spring, there was only one sample date in 1985, whereas there were 54 samples (TP range=0.009-0.147) from 1990 to 2003. There were no significant changes detected within the springs for orthophosphate.

I was concerned about the reliability of the total phosphorus data for Wakulla Spring (Wakulla Co.) in the early time period. Mean total phosphorus concentration decreased from 0.268 mg/L (range=0.04-1.05, N=11) in the early time period to 0.031 mg/L (range=0.030-0.032, N=2) in the recent time period. Total phosphorus data in the early time period for Wakulla Spring was collected by two different agencies, the United

States Geological Survey (USGS) and the Florida Department of Environmental Protection (FDEP). The USGS total phosphorus analysis revealed a concentration of 0.04 mg/L for Wakulla Spring in 1972 (sampling location unknown). The FDEP sampled Wakulla Spring 10 times from 1971-1975 from the dock near the spring and reported a mean total phosphorus concentration of 0.291 mg/L. This rather large difference in total phosphorus concentration (Figure 9) may have been a consequence of different sampling sites.

Percent variance analysis

In the percent variance analyses, 38 springs in the recent time period had ≥ 10 sampling dates for total phosphorus. A mean, median, and standard deviation percent variance of 52%, 36%, and 43% were calculated. Poe Spring (Alachua Co.), a 2nd magnitude spring, had the lowest percent variance of 19%, while Suwannee Spring (Suwannee Co.), another 2nd magnitude spring, had the highest percent variance of 119%. These calculations included 10 1st magnitude springs, 22 2nd magnitudes, and 6 3rd magnitude springs. Because of the relative lack of abundant data in the early time period, it is difficult to say whether any of the springs have actually changed with respect to total phosphorus. However, these analyses provide insight into the variability of total phosphorus in spring water when abundant data have been collected.

Time period analyses

Early time period vs. middle time period. In the time period comparisons, spring nutrient chemistries in each of the time periods displayed a wide range in concentrations (Table 4). In the early time period, the mean orthophosphate concentration (0.096 mg/L, N=29) was higher than the mean total phosphorus concentration (0.067 mg/L, N=28). This discrepancy is due to a difference in the number of springs used and that the same springs were not used in both analyses. There were no significant differences between mean values for total phosphorus or for orthophosphate in any of the time period comparisons (Table 5). However, in the early versus middle time period comparison, Warm Mineral (Sarasota Co.) and Blue (Madison Co.) Springs were outside of the calculated 95th percentile. Mean orthophosphate in these springs decreased from 0.4 mg/L to 0.03 mg/L and from 0.52 mg/L to 0.04 mg/L, respectively.

Early time period vs. recent time period. Although there was no significant difference between mean values of total phosphorus (Figure 10) or for orthophosphate in this time period comparison (Table 5), Siphon Creek Rise (Gilchrist Co.) was outside of the calculated 95th percentile. Total phosphorus in this spring increased from 0.02 mg/L to 0.09 mg/L.

Middle time period vs. recent time period. In the middle versus recent time period comparison, Cypress Spring (Washington Co.) was outside of the calculated 95th percentile. Total phosphorus in this spring decreased from 0.04 mg/L to 0.01 mg/L. Holton Creek Rise (Hamilton Co.) was outside of the 95th percentile for orthophosphate. Orthophosphate in this spring increased from 0.08 mg/L to 0.16 mg/L.

Although mean values for total phosphorus and orthophosphate did not statistically differ between time periods, it is clear that while some individual springs possibly exhibited increases in these nutrients, other springs may have exhibited decreases. Total phosphorus concentrations for the population of springs in the recent time period (N=94) ranged from 0.005 mg/L to 0.313 mg/L with a mean of 0.054 mg/L. In this time period, 82% of the springs had total phosphorus concentrations less than 0.080 mg/L, which suggests that significant sources of phosphorus, such as animal wastes, are not in close proximity to these springs (Jones et al. 1994). Total phosphorus concentrations within individual springs was, in many cases, highly variable (e.g., Convict- Lafayette Co.; 0.027 mg/L to 0.277 mg/L: Weeki Wachee- Hernando Co.; 0.011 mg/L to 0.477 mg/L) when there have been abundant data collected.

Nitrogen

Within-spring analyses

In the within-spring analyses, significant changes in nitrate-nitrogen concentration were detected in 18 out of 73 springs. Mean nitrate-nitrogen concentration (mg/L) increased in Wekiva (Levy Co.; 0.07 to 0.43), Blue (Madison Co.; 0 to 1.25), Crystal (Pasco Co.; 0.71 to 2.61), Cypress (Washington Co.; 0.15 to 0.28), Owens (Lafayette Co.; 0.50 to 3.64), River Sink (Wakulla Co.; 0.03 to 0.19), Turtle (Lafayette Co.; 0.42 to 0.66), Ichetucknee Head (Columbia Co.; 0.36 to 0.77), Branford (Suwannee Co.; 0.60 to 1.01), Fanning (Levy Co.; 0.35 to 3.82), Manatee (Levy Co.; 0.24 to 1.53), Ponce De Leon (Holmes Co.; 0.14 to 0.95), Bobhill (Hernando Co.; 0.03 to 0.66), Little (Hernando Co.; 0.08 to 0.81), Salt (Hernando Co.; 0.10 to 0.44), Weeki Wachee (Hernando Co.; 0.02 to 0.78), and Hart (Gilchrist Co.; 0.8 to 1.17) Springs. Fanning Spring (Levy Co.) provides a example of the increases in nitrate-nitrogen concentration (Figure 11). There was a significant decrease in nitrate-nitrogen in Hornsby Spring (Alachua Co.; 0.68 to 0.44). Due to the lack of historical data, total nitrogen data were not used in the spring analyses.

Percent variance analysis

In the nitrate-nitrogen percent variance analysis, 26 springs in the recent time period with ≥ 10 sampling dates were used. A mean, median, and standard deviation percent variance of 38%, 25%, and 37% were calculated. Ichetucknee Head Spring

(Columbia Co.), a 2^{nd} magnitude spring, had the lowest percent variance of 8.3%, while Falmouth Spring (Suwannee Co.), a 1^{st} order magnitude spring, had the highest percent variance of 158%. These calculations included 8 1^{st} magnitude springs, 17 2^{nd} magnitudes, and 1 3^{rd} magnitude spring. There was high variability in nitrate-nitrogen concentration in these springs with a mean range of 2.01 mg/L. Nitrate-nitrogen concentration in Fanning Spring (Levy Co.), a 1^{st} order magnitude spring, ranged from 2.35 mg/L to 8.74 mg/L in the recent time period (N=67). Of these 26 springs, 88% displayed a range ≥ 0.4 mg/L. Because of the relative lack of abundant data in the early time period, it is difficult to say whether any of the springs have actually changed with respect to nitrate-nitrogen concentration. However, these analyses provide insight into the variability of nitrate-nitrogen concentration in spring water when abundant data have been collected.

Interestingly, nitrate-nitrogen concentration in six of the 26 aforementioned springs increased from pre-1998 to 1998, then after 1998, nitrate-nitrogen concentration decreased. Temporal changes in nitrate-nitrogen concentration in Hornsby Spring (Alachua Co.) provide an example of the post-1998 decline (Figure 12). These patterns in nitrate-nitrogen concentration through time may reflect changes in hydrology, following a period of high rainfall in 1997 and 1998 (El Niño).

Three springs in the percent variance analyses displayed a significant increase in nitrate-nitrogen concentration in the within-spring analyses. Ichetucknee Head (Columbia Co.), Manatee (Levy Co.), and Hart (Gilchrist Co.) Springs exhibited increases in nitrate-nitrogen concentration outside of the calculated percent variance for those springs. These examples provide evidence that spring nitrate-nitrogen concentration is increasing in some springs.

Time Period Analyses

Early time period vs. middle time period. In the time period analyses, there was a statistically significant increase in mean nitrate-nitrogen concentration in the early versus middle time period comparison, with mean nitrate-nitrogen concentration increasing from 0.39 mg/L to 0.71 mg/L (Table 5).

Hornsby (Alachua Co.) and Blue (Madison Co.) Springs were outside of the calculated 95th percentile. Nitrate-nitrogen concentration increased in these springs from 0 mg/L to 0.68 mg/L and from 0 mg/L to 1 mg/L, respectively. Messant Spring (Lake Co.) was also outside of the calculated 95th percentile. Nitrate-nitrogen concentration decreased in Messant Spring from 1 mg/L to 0.01 mg/L.

Early time period vs. recent time period. In the early versus recent time period comparison, mean nitrate-nitrogen concentration increased from 0.46 mg/L to 1.04 mg/L (Table 5; Figure 13). Bell (Gilchrist Co.; 0 mg/L to 2.78 mg/L), Blue (Madison Co.; 0 mg/L to 1.25 mg/L), Hornsby (Alachua Co.; from 0 mg/L to 0.59 mg/L), Newport (Wakulla Co.; 1.8 mg/L to 0 mg/L) and Messant (Wakulla Co.; 1 mg/L to 0.01 mg/L) Springs were outside of the calculated 95th percentile.

Middle time period vs. recent time period. In the middle versus recent time period comparison, mean nitrate-nitrogen concentration increased from 0.86 mg/L to 1.10 mg/L, however this change was not statistically significant (Table 5). Blue (Jackson Co.) and Weeki Wachee (Hernando Co.) Springs were outside of the calculated 95th percentile. Nitrate-nitrogen concentrations increased in these systems from 1.29 mg/L to 3.30 mg/L and from 0.02 mg/L to 0.76 mg/L, respectively.

Increases in spring nitrate concentrations have been reported in many parts of Florida (e.g., Jones et al. 1996; Katz et al. 1999; Champion and DeWitt 2000; Champion and Starks 2001). In this study, 17 out of the 73 within-springs analyses with nitrate-nitrogen data pre- and post-1990, were found to have undergone significant increases in nitrate-nitrogen concentration, however, seven of the nine significant spring plots with ≥ 10 sampling dates in the recent time period showed significant decreases in nitrate-nitrogen concentration. Given the variance estimates for nitrate-nitrogen, some of the springs showing significant increases may have been fluctuating under natural variability.

The overall means for nitrate-nitrogen concentration in the early, middle, and recent time periods were 0.43 mg/L, 0.71 mg/L, and 1.13 mg/L, respectively (Table 4). Of the 1,254 total observations from 1907-2003, three percent of the nitrate-nitrogen concentrations were >5.00 mg/L, all occurring in the recent time period. A nitrate-nitrogen concentration of 10.3 mg/L occurred in Convict Spring (Lafayette Co.) in 1998. This was the only spring in which nitrate-nitrogen concentration exceeded the primary drinking water standard of 10.0 mg/L. Although mean nitrate-nitrogen concentration in the recent time period for Convict Spring (Lafayette Co.) was 7.54 mg/L, there was high variability in this spring (range: 0.11 mg/L to 10.3 mg/L). Historical data for nitrate in Convict Spring were not available and therefore it is unknown whether this spring has always displayed a relatively high mean nitrate-nitrogen concentration.

Table 1. Median pH and arithmetic mean for total specific conductivity, total alkalinity, chloride, total hardness, total phosphorus, orthophosphate phosphorus, total nitrogen and nitrate- nitrogen from 1990 to 2003. Total nitrogen data are from 1997 to 2003. N values represent the number of Florida springs used to calculate each value.

Analyte	Mean	Std. Dev.	N
pH	7.4	0.3	95
Total Specific Conductivity (µS/cm @ 25° C)	713	1211	90
Total Alkalinity (mg/L as $CaCO_3$)	137	43	55
Chloride (mg/L)	139	386	80
Total Hardness (mg/L as $CaCO_3$)	244	147	49
Total Phosphorus (mg/L)	0.054	0.043	94
Orthophosphate (mg/L as P)	0.046	0.038	25
Total Nitrogen (mg/L)	1.6	1.92	52
Nitrate-nitrogen (mg/L)	1.13	1.35	90

Table 2. Median pH and arithmetic mean values for total specific conductivity, total alkalinity, total chloride, and total hardness are in bold for a population of Florida springs. Standard deviations for each analyte are given and N values (number of springs) are in italics. N/A indicates data were not available for analyses

Time Period	pH	Total Specific Conductivity (µS/cm @ 25 C)	Total Alkalinity (mg/L as $CaCO_3$)	Total Chloride (mg/L)	Total Hardness (mg/L as $CaCO_3$)
	7.6	**1071**	**125**	**271**	**233**
Early (1907-1979)	0.4	3582	36	1245	446
	103	*104*	*102*	*106*	*104*
	7.3	**1233**	**124**	N/A	N/A
Middle (1980-1989)	0.4	4223	42	N/A	N/A
	35	*35*	*35*	N/A	N/A
	7.4	**713**	**137**	**139**	**244**
Recent (1990-2003)	0.3	1211	43	386	147
	95	*90*	*55*	*80*	*50*

Table 3. Median pH and arithmetic mean values for total specific conductivity (µS/cm @ 25° C), total alkalinity (mg/L as $CaCO_3$), total chloride (mg/L), and total hardness (mg/L as $CaCO_3$), for a population of Florida springs, are listed for each time period comparison (Early:1907-2003; Middle:1980-1989; Recent: 1990-2003). Paired t-tests that showed significant ($p<0.05$) difference are starred (*). N values represent the number of springs used in each comparison. N/A indicates data were not available for analyses.

Early Versus Middle Time Period Comparison

	Mean		
Analyte	Early	Middle	N
pH *	7.6	7.4	33
Total Specific Conductivity	1330	1260	34
Total Alkalinity	120	130	33
Total Chloride	N\A	N\A	N\A
Total Hardness	N\A	N\A	N\A

Early Versus Recent Time Period Comparison

	Mean		
	Early	Recent	N
pH *	7.6	7.4	91
Total Specific Conductivity *	610	730	87
Total Alkalinity *	120	140	54
Total Chloride	6.0	5.8	79
Total Hardness *	190	240	49

Middle Versus Recent Time Period Comparison

	Mean		
	Middle	Recent	N
pH	7.3	7.4	25
Total Specific Conductivity *	570	620	25
Total Alkalinity	130	130	9
Total Chloride	N\A	N\A	N\A
Total Hardness	N\A	N\A	N\A

Table 4. Arithmetic mean of total phosphorus, orthophosphate, and nitrate-nitrogen are in bold, for a population of Florida springs, for each time period (Early:1907-1979; Middle:1980-1989; Recent:1990-2003). Range values are in parentheses and N values (number of springs) are in parentheses and N values (number of springs) are in italics.

Time Period	Total Phosphorus (mg/L)	Orthophosphate (mg/L as P)	Nitrate-nitrogen (mg/L as N)
	0.067	**0.096**	**0.43**
Early (1907-1979)	(0.01-0.42)	(0.01-0.52)	(0-5.0)
	28	*29*	*87*
	0.055	**0.046**	**0.71**
Middle (1980-1989)	(0.02-0.16)	(0.01-0.15)	(0.01-3.2)
	35	*35*	*35*
	0.054	**0.046**	**1.13**
Recent (1990-2003)	(0.005-0.313)	(0.01-0.16)	(0-7.54)
	94	*25*	*90*

Table 5. Arithmetic means of total phosphorus (mg/L), orthophosphate (mg/L), and nitrate-nitrogen (mg/L), for a population of Florida springs, are listed for each time period comparison (Early: 1907-1979; Middle: 1980-1989; Recent: 1990-2003). Paired t-tests that showed significant ($p<0.05$) difference are starred (*). N values represent the number of springs used in each comparison.

Early Versus Middle Time Period Comparison

	Mean		
Analyte	Early	Middle	N
Total Phosphorus	0.060	0.054	20
Orthophosphate Phosphorus	0.092	0.044	19
Nitrate Nitrogen *	0.39	0.71	31

Early Versus Recent Time Period Comparison

	Mean		
	Early	Recent	N
Total Phosphorus	0.072	0.062	23
Orthophosphate Phosphorus	0.099	0.031	15
Nitrate Nitrogen *	0.46	1.04	69

Middle Versus Recent Time Period Comparison

	Mean		
	Middle	Recent	N
Total Phosphorus	0.056	0.058	26
Orthophosphate Phosphorus	0.046	0.050	17
Nitrate Nitrogen	0.86	1.10	24

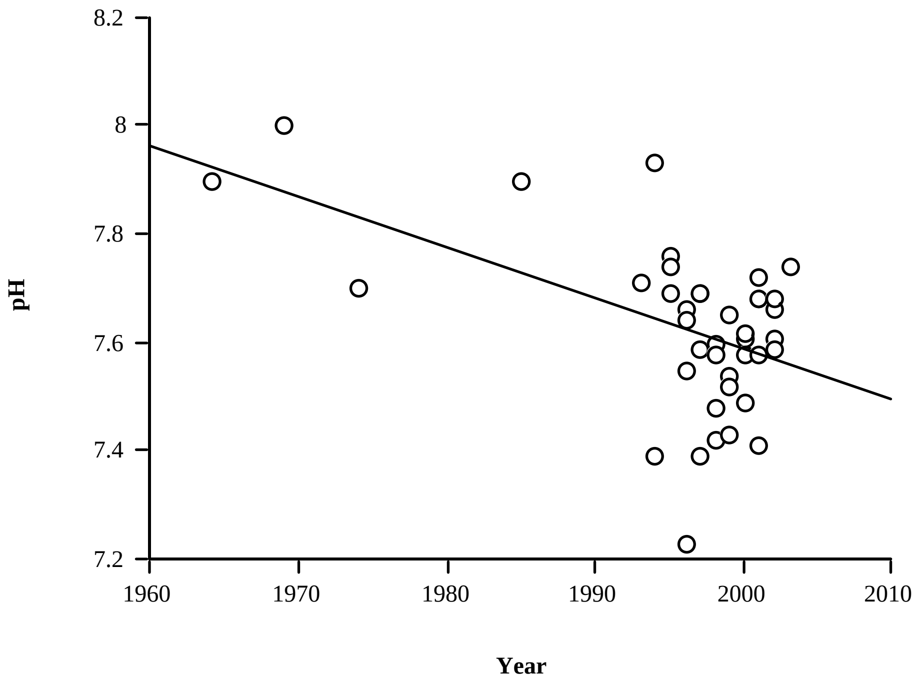

Figure 1. Simple liner regression of pH by year (r^2=0.263, df=39, p<0.0001) for Weeki Wachee Spring (Hernando Co., Florida), with regression line (—).

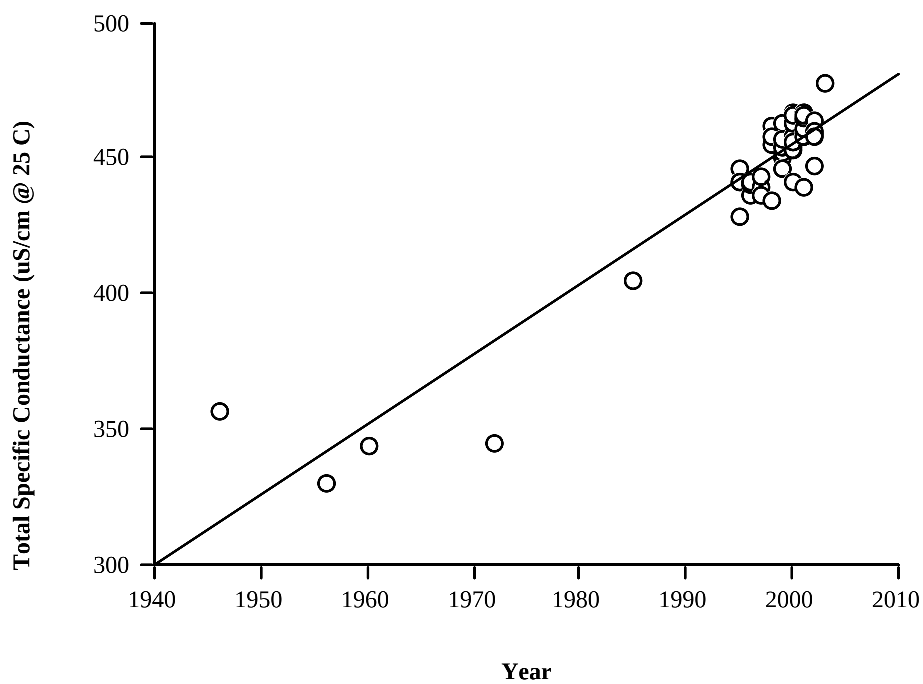

Figure 2. Simple linear regression of total specific conductivity by year (r^2=0.88, df=56, p<0.0001) for Fanning Springs (Levy Co., Florida), with regression line (—).

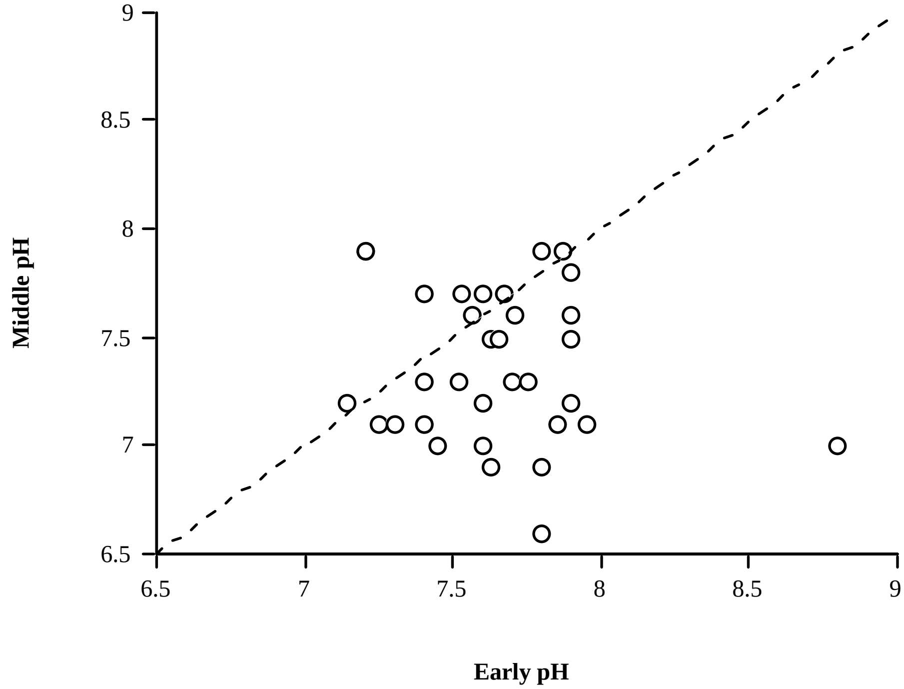

Figure 3. Relationship between early time period (1907-1979) pH and middle time period (1980-1989) pH, with a 1:1 line (- -), for 33 Florida springs.

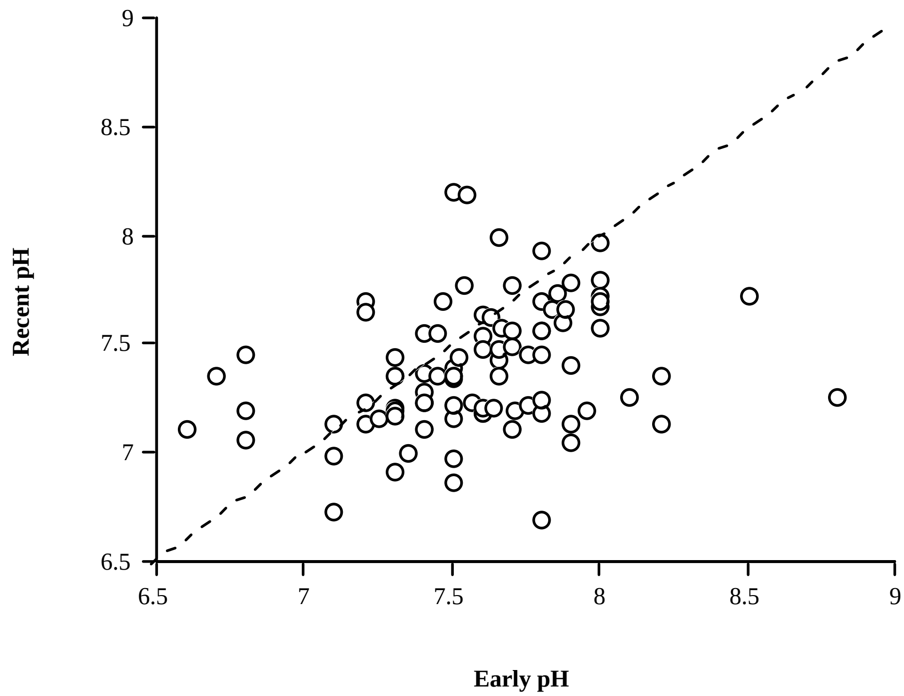

Figure 4. Relationship between early time period (1907-1979) pH and recent time period (1990-2003) pH, with a 1:1 line (- -), for 91 Florida springs.

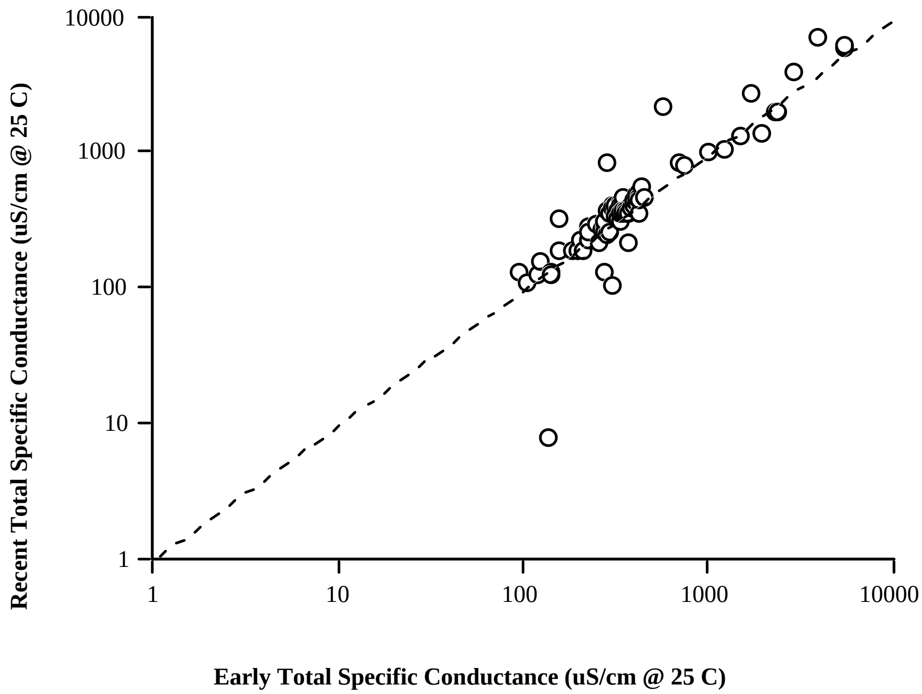

Figure 5. Relationship between early time period (1907-1979) total specific conductivity and present time period (1990-2003) total specific conductivity, with a 1:1 line (- -), for 87 Florida springs.

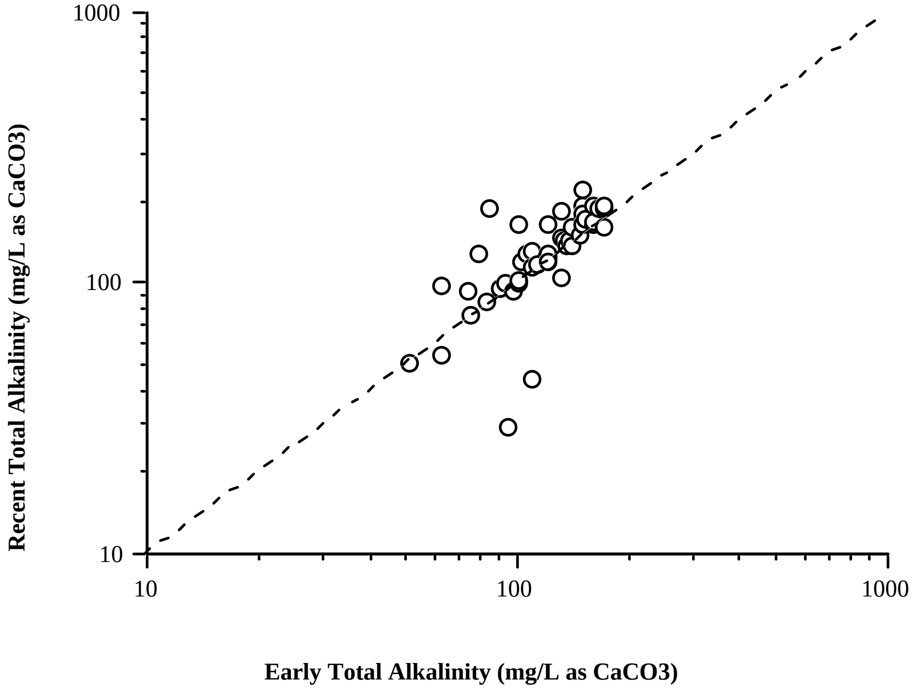

Figure 6. Relationship between early time period (1907-1979) total alkalinity and recent time period (1990-2003) total alkalinity, with a 1:1 line (- -), for 54 Florida springs.

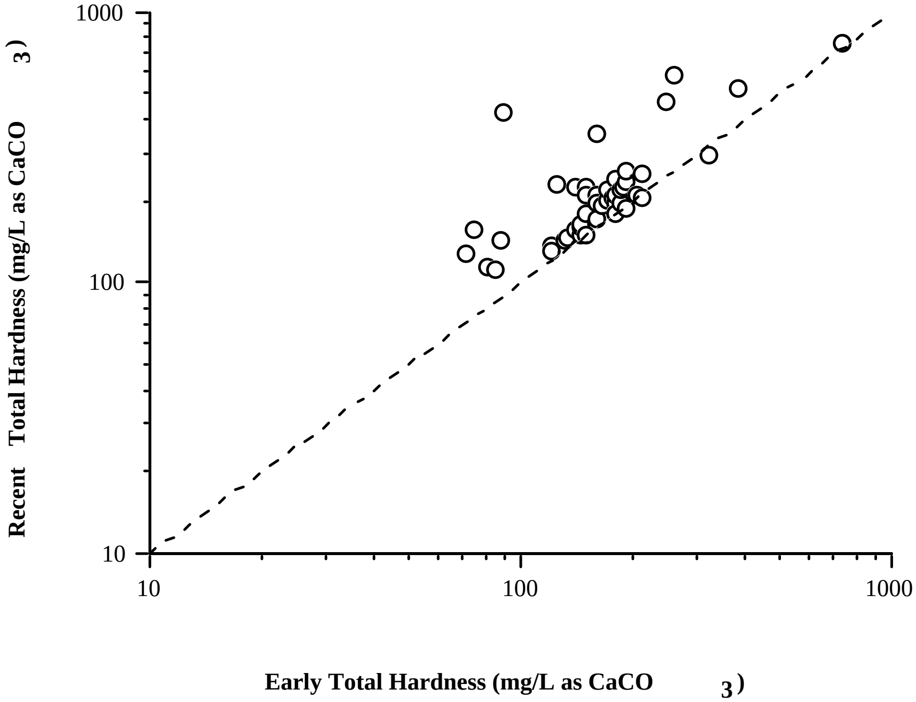

Figure 7. Relationship between early time period (1907-1979) total hardness and recent time period (1990-2003) total hardness, with a 1:1 line (- -), for 49 Florida springs.

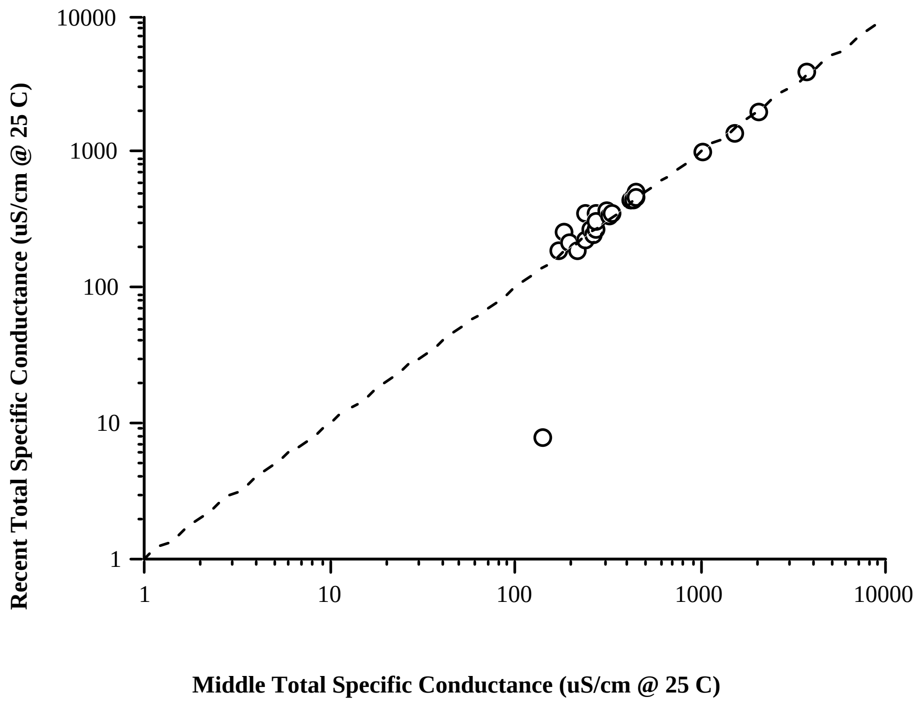

Figure 8. Relationship between middle time period (1980-1989) total specific conductivity and recent time period (1990-2003) total specific conductivity, with a 1:1 line (- -), for 25 Florida springs.

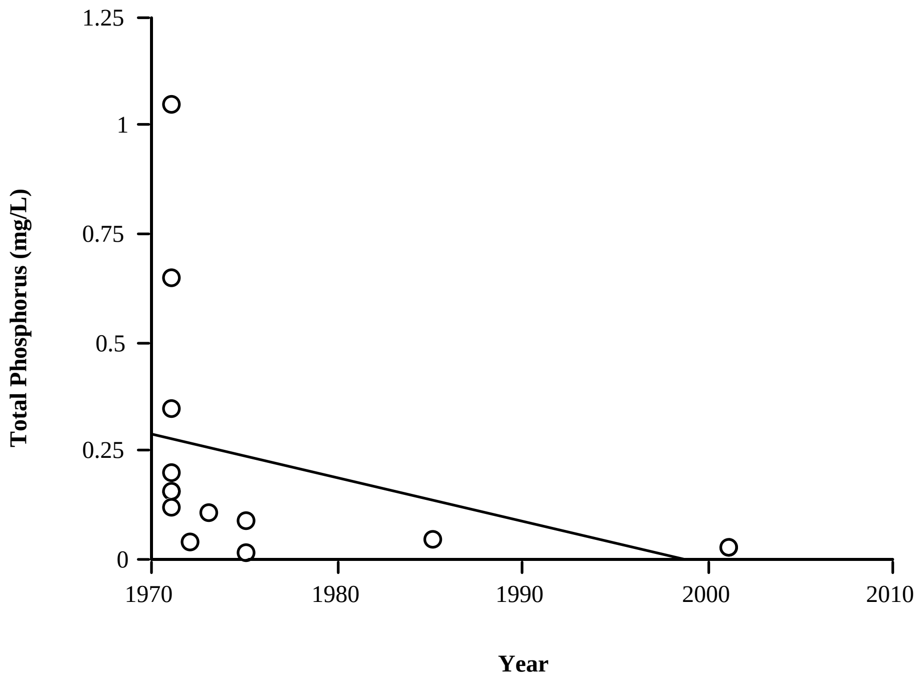

Figure 9. Simple linear regression of total phosphorus concentration by year (r^2=0.14, df=13, p=0.1882) for Wakulla Spring (Wakulla Co., Florida), with regression line (—).

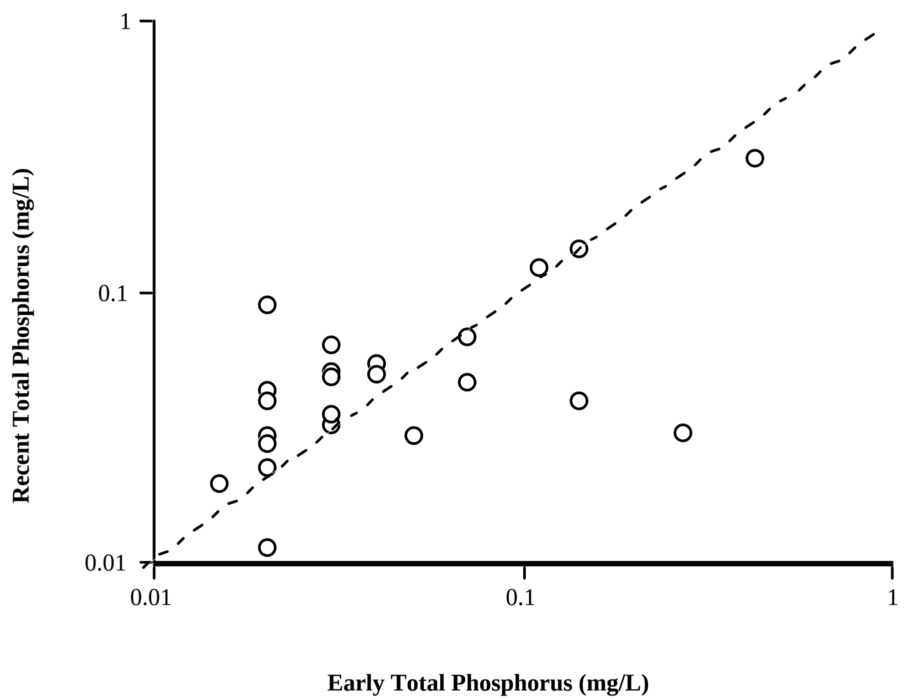

Figure 10. Relationship between early time period (1907-1979) total phosphorus and recent time period (1990-2003) total phosphorus, with a 1:1 line (- -), for 23 Florida springs.

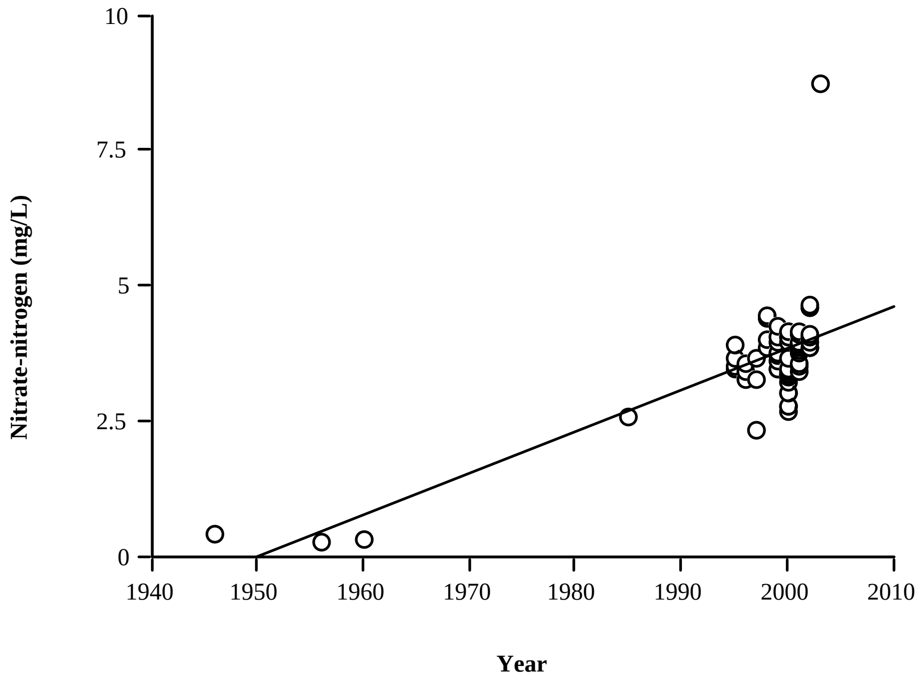

Figure 11. Simple linear regression of nitrate-nitrogen concentration by year (r^2=0.523, df=69, p<0.001) for Fanning Springs (Levy Co., Florida), with regression line (—).

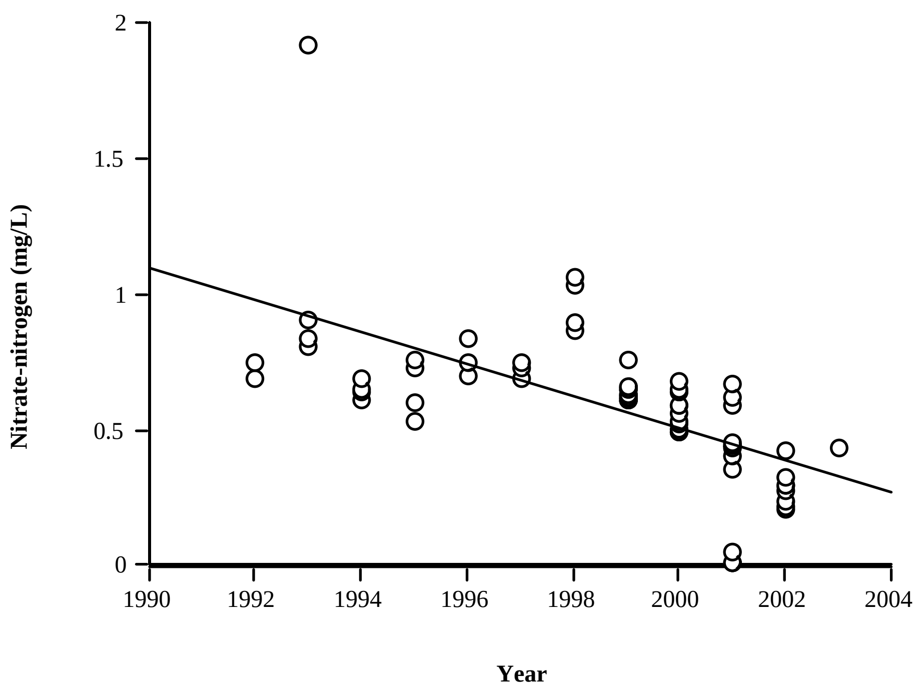

Figure 12. Simple linear regression of nitrate-nitrogen concentration by year (r^2=0.055, df=75, p=0.042) for Hornsby Spring (Alachua Co., Florida).

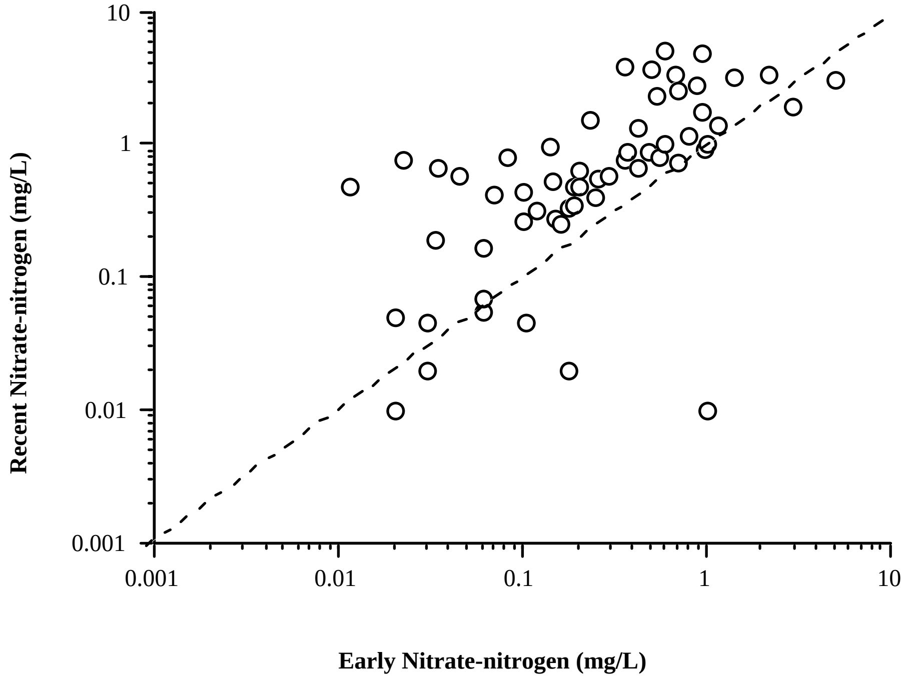

Figure 13. Relationship between early time period (1907-1979) nitrate-nitrogen and recent time period (1990-2003) nitrate-nitrogen, with a 1:1 line (- -), for 69 Florida springs.

CHAPTER 4
CONCLUSION

Although statistically significant temporal changes in median pH, and mean values for total specific conductivity, total alkalinity, total hardness, and nitrate-nitrogen concentrations were detected within individual springs and within the population of springs, these changes may have been influenced by differences in methodology or the paucity of historical data, and not from actual increases or decreases in the water chemistry analytes. Methodological differences include changes in sampling protocols, sampling sites, and laboratory analyses. Rosenau et al. (1977) collected water samples as close as possible to the springs' orifices, vents, seepage zones, or other points of spring discharge, except for spring groups, which were sampled downstream. Southwest Florida Water Management District used stationary sampling tubes and peristaltic pumps that were placed at the vent, to collect in situ samples, whereas I collected composite water samples from just below the surface (ca. 0.5 m).

Because this study covered such a broad time scale (96 years), changes in methodologies and rainfall, may have influenced the results. Given these changes have occurred, I have shown significant changes in some spring water chemistries through time. The variability of spring chemistries in the early and middle time periods is not known due to the paucity of data; therefore, the results from the individual spring and spring population analyses in this study were difficult to interpret. Most importantly, because most springs in the early time period had only one or two sampling dates, the uncertainty surrounding the nitrate-nitrogen analyses, as well as the other chemical analyses, was high.

Degradation of ground-water quality, associated human health concerns, and increases in nuisance growths of aquatic macrophytes, in the springs and downstream, are the major concerns with respect to Florida's springs. However, in the recent time period, only two of the 90 springs expressed mean nitrate-nitrogen concentrations greater than 5 mg/L. Therefore, if these springs adequately reflect ground-water chemistries, the potential for ground-water induced infant methemoglobinemia is low.

Florida's springs continue to provide an invaluable natural resource to fish, wildlife and the citizens and visitors of Florida. Although Florida's population has increased an estimated 150% since 1970 (U.S. Bureau of the Census 2002), I did not detect a significant increase, in the within-population analyses, for total phosphorus; a nutrient often associated with eutrophication from urban development (Wetzel 1983; Ryding and Rast 1989, Barbiero et al. 2002) and agriculture (Hutchinson 1957; Jones et al. 1997). However, significant increases in nitrate-nitrogen concentration were detected within individual springs and within this population of springs.

Because the concerns over eutrophication and infant methemoglobinemia are not going to diminish, monitoring of spring and ground-water chemistries should continue. If costs interfere with continued agency monitoring, citizen monitoring programs like the University of Florida's LAKEWATCH program, should be implemented. Citizen monitoring may provide for a more widespread and abundant database of Florida's springs, which could include water chemistry and aquatic plant sampling (Florida LAKEWATCH 2002).

APPENDIX A
GENERAL CHEMISTRY RAW DATA

These data are for a sample population of Florida springs (N=107), with sampling dates ranging from 1907 to 2003. These data were used to assess potential changes in water chemistry within individual springs (linear regression) and within a population of Florida springs (paired t-tests).

Object 1. Excel spreadsheet data of general chemistry raw data for springs located by county. (appendix-a-excel.xls, 504 KB)

Object 2. Comma Separated Variable (CSV) version of spreadsheet data of general chemistry raw data for springs located by county. (appendix-a-comma.csv, 97 KB)

Object 3. Tab delimited text version of spreadsheet data of general chemistry raw data for springs located by county. (appendix-a-text.txt, 97 KB)

APPENDIX B
NUTRIENTS RAW DATA

These data are for a sample population of Florida springs (N=109), with sampling dates ranging from 1907 to 2003. These data were used to assess potential changes in water chemistry within individual springs (linear regression) and within a population of Florida springs (paired t-tests).

Object 4. Excel spreadsheet data of nutrient raw data for springs located by county. (appendix-b-excel.xls, 770 KB)

Object 5. Comma Separated Variable (CSV) version of spreadsheet data of nutrient raw data for springs located by county. (appendix-b-comma.csv, 132 KB)

Object 6. Tab delimited text version of spreadsheet data of nutrient raw data for springs located by county. (appendix-b-text.txt, 132 KB)

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BIOGRAPHICAL SKETCH

William Aaron Strong was born and raised in Tallahassee, Florida. He graduated from Leon High School in 1996. He received his Bachelor of Science degree in animal science from the University of Florida in 2002. While finishing his undergraduate studies, he gained employment in May 2000, as a technician at the Florida Fish and Wildlife Conservation Commission (FFWCC) working with the American Alligator (*Alligator mississippiensis*). Upon finishing his undergraduate degree, he entered the fisheries and aquatic sciences graduate program at the University of Florida where he conducted research on the chemical characteristics of Florida springs. After completion of his graduate research, he will continue to work at the University of Florida as a biological scientist directing his focus on the Lake Tohopekaliga habitat enhancement project.