TREND ANALYSES OF GROUNDWATER QUALITY IN THE UPPER FLORIDAN AQUIFER OF ALACHUA COUNTY, FLORIDA (1987-2021)

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EXECUTIVE SUMMARY

Nitrate concentrations in groundwater have been a concern of the Alachua County Environmental Protection Department (ACEPD) for decades. As a partial response, ACEPD established a groundwater quality monitoring network (GWQMN) in 1987. This report summarizes how concentrations of monitored indicators have changed since the late 1980s.

Groundwater quality data, obtained from the GWQMN was analyzed for statistical trends. Data obtained from 1987 through 2021 (35 years) were used in the evaluations. The individual indicators are listed in Table 1. Based on the frequency of data collection by ACEPD, data were grouped into three periods: Early (1987-1999), Middle (2000-2008) and Late (2009-2021). Data from the Middle period were relatively scarce, and for this reason, were not used for data analyses. Nevertheless, visual comparisons of data from the Middle period were compared to the Early and Late periods. Regarding Early and Late period data, two types of trend analyses were performed. Step trend analyses compared annual means and annual medians between the Early and Late periods. If changes occurred they are reported as either an upward or downward step. Monotonic, time-series, compared annual means and medians data over the Later period, where data were sufficient to conduct time-series trend analyses.

Step and monotonic trend analyses were conducted for each analyte, first by treating each well separately (trend analyses at each well) and second by treating all wells as a group. Emphasis was given to latter type of analyses to analyze for "big picture" county-wide trends in the Upper Floridan aquifer (UFA), the major aquifer within the county. County-wide comparisons of data from the Early (1987-1999) to Late (2009-2021) periods revealed that concentrations of alkalinity (Alk), calcium (Ca), potassium (K), and sodium (Na) increased. Of note, nitrate (NO3) concentrations did not change. Regarding the monotonic trend analyses during the Late period, concentrations of Ca and K continued to increase whereas dissolved oxygen (DO) concentrations decreased. Again, no observable changes in NO3 concentrations were observed.

Concentration changes of Alk, Ca, K, and Na are possibly related to annual precipitation (rainfall). Copeland and Woeber (2021) observed that on the statewide scale, during the 1990s and continuing through the mid to late 2000s, Florida's annual rainfall decreased. During this time, concentrations of these analytes increased over most of Florida in the UFA. Copeland and Woeber hypothesized that if a long period of declining rainfall is followed by several years of annual increases in rainfall, concentrations of these indicators will eventually begin to decrease. Concerning Alachua County, note that from the mid-1980s through the late 2000s, rainfall decreased. Beginning in about 2011, and continuing through 2021, rainfall increased. During this period, concentrations of Ca and K continued to increase. However, Alk and Na leveled off. It is predicted that if annual rainfall continues to increase, concentrations of Ca and K will level off, and eventually, concentrations of all four analytes will decline.

Regarding DO concentrations, during the Late period, they declined. Upchurch (1992) indicated that DO concentrations are dependent on temperature. The US Geological Survey (USGS, 2023) mentioned that as temperature increases, DO concentrations tend to decrease in groundwater. During the Late period, air temperature across Florida increased (Florida Climate

Center, 2023). In addition, the authors discovered that from the Generalized Water Information System database from the Florida Department of Environmental Protection (FDEP), groundwater temperatures across Florida increased.

A secondary purpose for initiating this project was to conduct a gap analysis regarding the design of the GWQMN. It turns out that to conduct the most efficient analyses for trends, data need to be independent. Imagine two wells located next to each other, say 10 feet. Both wells are drilled to the same depth within the UFA. Suppose the two wells were sampled at the same time. It is reasonable to assume the resulting analyte concentrations have almost the same values. In this situation, data are considered dependent. However, if both samples are sufficiently separated in time, and if the wells are located sufficiently far enough from each other in space, the resulting concentrations will be considered independent. Concentrations would not necessarily be expected to have similar concentrations. For these reasons, data from any monitoring network needs to be independent. If they are not, then it is possible that the results of trend analyses are invalid. Thus, the ACEPD desires to have a network in which sample data are independent both in time and space.

Copeland and Woeber (2021) found that if annual means and medians are used in analyses, in terms of time, the values are rarely dependent. In addition, during this investigation, it was discovered that analyte concentrations in the UFA become independent at about 14,373 feet. ACEPD used this information to construct a series of county maps overlain with hexagons of various diameters, each greater than 14,373 feet. For each map, ACEPD overlaid a map of the Alachua County well network. Hexagons without current network wells become target areas for future "fill-in" wells. Seeking to minimize the cost of adding wells plus the cost of sample collection and analysis, ACEPD suggested a 30,000 ft hexagon grid. If so, there are five hexagons in the unconfined portion of Alachua County needing a monitoring well.

INTRODUCTION AND PURPOSE

Unfavorable environmental impacts to both groundwater and surface water from nitrogen-based nutrients have been a concern in Alachua County, Florida (Figure 1) and across Florida for years. Of particular concern is nitrate. Concentrations in the UFA have increased for the past several decades (Florida Springs Task Force, 2000; Upchurch et al., 2019). As a partial response in 1987, the ACEPD established and began operation of its GWQMN. The network monitors nitrate and other indicators (analytes) in the aquifer. The purpose of the monitoring is to determine if groundwater quality in the UFA is changing over time.

In the summer of 2023, AquiferWatch Inc. entered into an agreement with ACEPD to analyze the groundwater quality data generated by the GWQMN. The purpose of this investigation was to: (1) determine if indicator concentrations changed over time within the UFA, if so, (2) discuss plausible causes (drivers) of the changes, and (3) provide a map for potential future wells to be added to the network in areas where wells are not currently located (gap analysis).

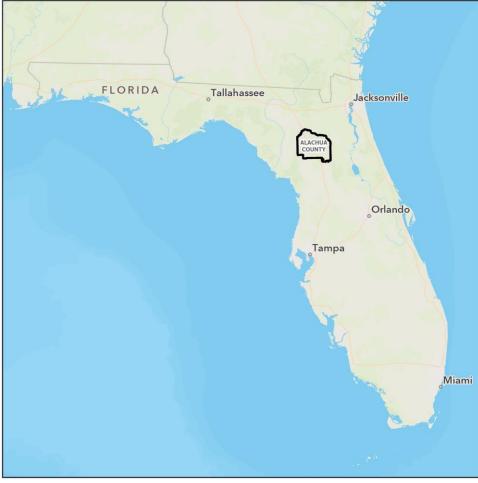


Figure 1. Location of Alachua County in Florida.

UPPER FLORIDAN AQUIFER

Underlying Alachua County are three freshwater aquifer systems. From deep to shallow they are: (1) the Floridan aquifer system, (2) the intermediate aquifer system and confining unit, and (3) the surficial aquifer system (Southeastern Geological Society (SEGS, 1986)). The largest in terms of groundwater use is the Floridan aquifer system, which is made up of the Lower Floridan aquifer, the Middle Confining units, and the Upper Floridan aquifer (UFA). The UFA is the aquifer of most concern for at least two reasons: (1) it is the aquifer used by the county with the most groundwater abstraction, and (2) it is vulnerable to groundwater contamination (e. g. nitrate), especially in the western portion of the county. The vulnerability is partially due to a lack of a confining unit in the west. That is, the UFA is under unconfined conditions. A semi-protective, perforated, confining layer of sediments overlies the UFA in the central portion of the county (Figure 2). The eastern part of the county the UFA is mostly overlain by impermeable sediments that confine the aquifer. The confinement assists protecting the aquifer from contaminants originating at land surface. According to the Southeastern Geological Society, the UFA is a carbonate sequence which includes all or parts of Paleocene to early Miocene formations. Regarding the entire Floridan aquifer system, Miller (1986) and Williams and Kuniansky (2016) indicated it is one of the most productive aquifer systems in the world. It underlies all of Florida and portions of South Carolina, Georgia, and Alabama. Klein (1975) mentioned that it can be over 900 meters (2950 feet) thick in places. Scott (2016), along with Budd and Vacher (2004), mentioned that the aquifer system acts as a multi-porosity aquifer: fractured and porous where it is confined and karstic, fractured, and porous where it is unconfined.

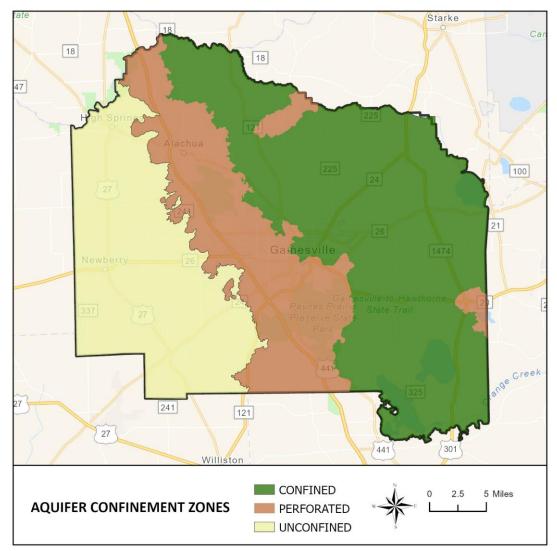


Figure 2. Confinement of the Upper Floridan aquifer in Alachua County.

METHODOLOGY

Indicators

Twelve indicators were used for the analyses. Data covered 35 years between 1987 and 2021. The indicators are displayed in Table 1, along with their corresponding abbreviations used in this report, measuring units, and drinking water standards if applicable. Standards will be

discussed shortly. During the evaluation period, indicators were measured as either dissolved (water samples passed through a 45-micron filter in the field prior to laboratory analysis) or total (not filtered in the field). Most samples were total, and to make each indicator time series as complete as possible the dissolved samples were treated as if they were total. For brevity, whenever practical, indicators will be referred to by their abbreviations.

Of the 12 indicators in Table 1, four have U.S. EPA drinking water standards (DWS) (U.S. Environmental Protection Agency, 2023) that represent maximum contaminant levels. Primary drinking water standards (PDWS) are based on health criteria. Of the indicators in Table 1, only sodium and nitrate plus nitrite as N have PDWSs. They are 160 and 10 mg/L, respectively. Secondary drinking water standards (SDWS) are based on aesthetic criteria, such as taste or smell. The two indicators with SDWS are chloride (Cl) and sulfate (SO4), both with a limit of 250 mg/L. For a discussion of each indicator, see Hem, 1985. The author presents a good discussion regarding the chemical characteristics of each indicator as found in natural waters. Other indicators in Table 1 are Alk, ammonia (NH3), Ca, DO, K, magnesium (Mg), total Kjeldahl nitrogen (TKN), and total nitrogen (TN).

| Indicator/Analyte | Abbreviation | Unit | DWS ⁴ |
|---|--------------|------|-----------------------|
| Alkalinity (D ¹ and T ²) | Alk | mg/L | |
| Ammonia (D and T) | NH3 | mg/L | |
| Calcium (T) | Ca | mg/L | |
| Chloride (T) | Cl | mg/L | 250 mg/L ⁶ |
| Dissolved Oxygen (Field ³) | DO | mg/L | |
| Potassium (T) | K | mg/L | |
| Magnesium (T) | Mg | mg/L | |
| Nitrate as N (T) | NO3 | mg/L | 10 mg/L^5 |
| Sodium (T) | Na | mg/L | 160 mg/L^5 |
| Sulfate (T) | SO4 | mg/L | 250 mg/L ⁶ |
| Total Kjeldahl Nitrogen (T) | TKN | mg/L | |
| Total Nitrogen (T) | TN | mg/L | |

Table 1. Indicators and analytes used in this investigation.

 1 D – Dissolved 2 T – Total 3 Field – Obtained in the field. 4 DWS – Drinking Water Standard 5 Primary 6 Secondary

Preliminary Analysis and Data Preparation

Several software platforms and packages were used for this project. They include the R statistical platform of packages (R Core Team, 2023), the statistical software package NCSS (2023), ArcGIS Pro (ESRI, 2023), and the Excel package in Microsoft 365 (Microsoft, 2023).

During preliminary evaluation, groundwater data fell into four groups based on sampling years (Table 2). Raw data are in Appendix A. From 1987 through 1999, the data represents 11.2% of the total 5,924 samples used for the project. These data contained missing data in several of the years. The 2000-2008 data set (3.5% of the total) contains numerous missing data. During 2007-2008, data were mostly obtained in a pre-determined wet season (June-November) but rarely in the pre-defined dry season (December-May). The 2009-2021 data set contains 85.3% of the total number of samples with only a few missing data. Based on the groupings in Table 2, data were separated into three groups: Early, Middle, and Late. The Early period is 1987-1999, the Middle

period is 2000-2008, and the Late period is 2009-20210. Often in this report, reference is given to the entire period (1987-2021).

| Period | Name | Number of samples (n) | Percent of Total | Comment |
|-----------|--------|--------------------------|---------------------|---------------------------|
| 1987-1999 | Early | 664 | 11.2 | Periodically missing data |
| 2000-2008 | Middle | 205 | 3.5 | Missing many data |
| 2009-2021 | Late | 5055 | 85.3 | Good set of data |

 Table 2. Grouping of Data Based on Years Data Collected.

In an ideal world, data are collected at equal time frequencies (e. g. years, seasons, quarters, months). For management and economic reasons, ACEPD was not able to collect data each year. To assist in data interpretation, two types of plots of data were constructed for each indicator: time-series plots and boxplots. Time-series plots were constructed for the entire period and the Late period (2009-2021). Recall that a high proportion of missing data exists in the Early and Middle periods.

For each time-series plot, the corresponding annual mean (average) and annul median are displayed. To obtain the median of an indicator, all data are sorted from smallest to largest. The middle value is the median. Environmental data are often "skewed positive." That is, relative to low values, there are numerous high values. The resulting data distributions are not normal or "bell-shaped". For this reason, nonparametric statistical procedures are needed n for trend analyses (Conover, 1999). The procedures will be discussed shortly.

Figure 3 is a time-series for alkalinity (Alk) for the entire study. Appendix B contains annual mean and median values and time-series plots of each indicator. In Figure 3, the median values are in the burnt-orange color. The mean values are in blue. The burnt orange dotted line represents the best fit line (Triola, 1998). The line slopes upward but is not necessarily statistically significant. Significance is based on the results of the corresponding statistical procedures and will be discussed later. Note that between 1987 and 1999, data were available for Alk in only four of those years.

Figure 4 displays similar information as found in Figure 3, except the series is constrained to the 2009-2021 period, or the Late period. Plots analogous to Figures 3 and 4 for each indicator are found in Appendix B.

Figure 5 is also an example of a time-series plot, but for sodium (Na). In the figure, note the mean values (blue), especially during the Late period. If one were to construct a "best-fit" trend line on mean data, the slope line would increase at a greater rate than the slope line for the median values (the one displayed). For this reason, only medians were used for trend detection analysis. Trend analyses results using medians are more conservative than using means. That is, trend detection procedures are less likely to result in a significant trend if medians are used, relative to means on skewed data.

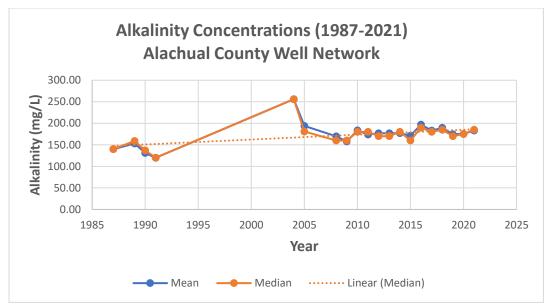


Figure 3. Alkalinity Concentrations (1987-2021), the Entire Period of Record.

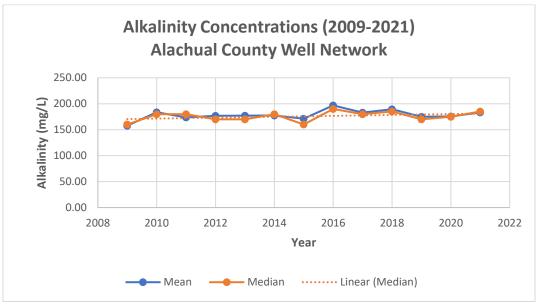


Figure 4. Alk Concentrations (2009-2021), the Late Period.

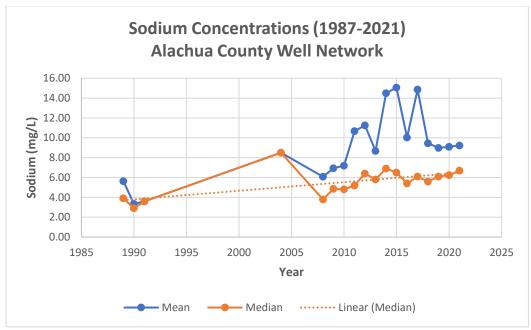
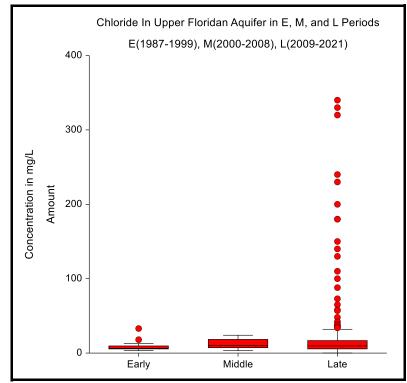


Figure 5. Sodium (Na) Concentrations (1987-2021), the Entire Period of Record

Inspection of Figures 3 and 5 displays the considerable amount of missing data in both the Early and Middle periods. To conduct trend analyses for the entire period of the study, step trend analysis can be used. Step trend analysis can be used to compare data between two periods of time. Lindsey and Rupert (2012) mentioned that because of the velocity of surface water flow compared to groundwater, the two periods can be continuous. However, because relative to surface water, groundwater velocity is slow, a gap in time of at least three years between the two periods is needed if possible. For this project, step trend analyses were conducted between the Early and Late periods for each analyte. In addition, boxplots (Triola, 1998) were used to visually assist in data interpretation. Data from the Middle period was not used for data analyses, but it is important to visually inspect the Middle data. For this reason, boxplots were constructed for each indicator and include data from all periods.

Figure 6 is an example boxplot. Chloride (Cl) data for all periods are represented. Data in each box represents the middle 50% of the data. The bottoms of the boxes represent the 25^{th} percentile or P₂₅. The tops of the boxes represent P₇₅ and the black horizontal line within each box represents P₅₀ (the median). The black horizontal lines below and above, but outside, of the boxes represent P₀₅ and P₉₅, respectively. The red circles represent outliers (unusual values) (Triola, 1998). Note the high number of upper outliers, and in this situation, no lower outliers. While inspecting boxplots, it is occasionally better to exclude the outliers from the plots, and this was done for all remaining indicator boxplots. Figure 7 is an example and displays an advantage excluding outliers from the plots. Inspection of the figure reveals that Cl concentrations increased from the Early to the Middle period and then leveled off in the Late period. Boxplots for each indicator are found in Appendix B.

Figure 8 is another example for the use of boxplots. In the figure, notice that total nitrogen (TN) has no data in the Early period. Also, concentrations of TN appear to have decreased from



the Middle to the Late period. Note, concentrations changes in the time-series and boxplots do not necessitate statistical trends.

Figure 6. Boxplots of Early, Middle, and Late data for Chloride.

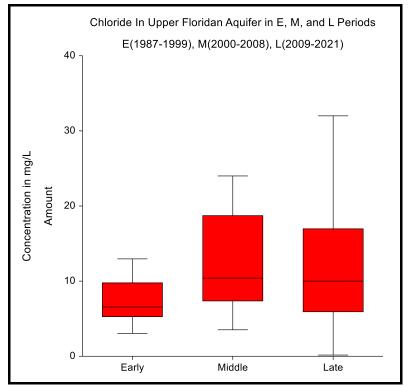


Figure 7. Boxplots of Early, Middle, and Late data for Chloride, excluding outliers

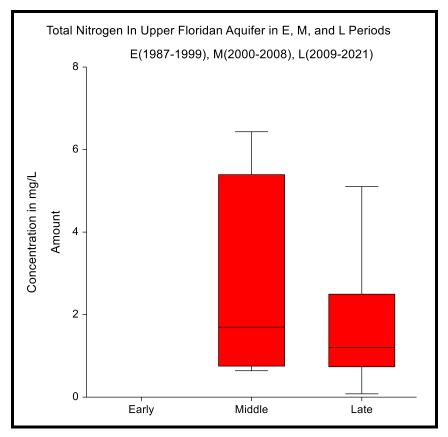


Figure 8. Boxplots of Early, Middle, and Late data for Total Nitrogen. No data available in Early period.

Trend Analyses Procedures

<u>Wilcoxon Signed Rank (WSR) Test</u>. The WSR test is a two-sided, two-sample (e. g. Early and Late), step-trend test. It is used for dependent matched pairs. The test is discussed thoroughly by Conover (1999) and Triola (199). For this investigation, the test was used to determine if the median concentrations of an indicator are different between the two time periods for matched pairs of monitoring sites <u>as a group</u>. For each indicator, the WSR test was used to compare data between the Early and Late periods. However, only 10 of the 24 sites were sampled during both the Early and the Late periods. The results of the small "n" size (10) affected statistical analyses. For a statistical trend to be observed in a small sample size, a larger difference in the magnitude of change is generally needed.

For each indicator, the WSR test uses the differences between each matched pair of sites. It is assumed that the distribution of the differences is approximately symmetric. For the twosided test, the null hypothesis (NH) is, no difference in the distribution of concentrations, including the median, between the Early and Late periods. The alternate hypothesis (AH) is, there is a change. The NH is rejected if the probability of the NH is ≤ 0.05 (5%). That is, there is only a 5% or less probability that the NH is true. <u>Mann-Whitney (MW) Test</u>. The test is sometimes referred to as the Wilcoxon Rank Sum test. For this investigation, the MW terminology will be used to not confuse it with the WSR test. The MW test is a two-sided, two-sample, step-trend test. It is discussed by Conover (1999) and Triola (199). The test was used to determine if the distribution of concentrations, including the median, changes between two time periods <u>at each individual monitoring site</u>.

The test assumes that the individual samples are independent, both between and within the two time periods. Independence between the two interludes is assumed because there is a minimum gap of three years between the two periods (Lindsey and Rupert, 2012). Independence within either the Early or Late periods will be discussed later. The null hypothesis is there is no difference in the distributions, including the median concentrations, between the Early and Late periods. The alternate hypothesis is there is a change. The NH is rejected if the p-value is ≤ 0.05 .

<u>Regional-Kendall (RK) Test</u>. This test is a monotonic time-series trend test. It examines changes in the concentration slope over time. Helsel and Frans (2006) discuss the procedure in detail. The motive for deriving the test was to address serial and spatial autocorrelation (AC). Both types of AC can adversely affect the outcome of trend tests. This issue will be discussed in more detail shortly. Regarding the RK test, Helsel and Frans indicated that the test accounts for both types of AC. The test adequately addresses serial correlation by accounting for seasonality. However, the test works better if the sampling design assists in accounting for spatial AC. ACEPD is making efforts to improve their network design to address spatial AC. The test was used to determine if, over a time-series, a statistical trend is observed for <u>all monitoring sites as a group</u> for a given indicator. The NH is the slope of concentrations over time is zero, while the alternative hypothesis is one of no change. The NH is rejected if the resulting p-value is ≤ 0.05 .

<u>Seasonal-Kendall (SK) Test.</u> This test was developed and is discussed by Hirsch and Slack (1984). As with the RK, the test is a monotonic time-series test that is often used with nonparametric data. It accounts for seasonal autocorrelation (AC) which the authors mention is the most significant source of serial AC for most environmental data. For the ACEPD data, the two seasons are: (1) dry (December-May) and wet (June-November). The test was used to determine if, for each indicator, a statistical trend was <u>observed for each monitoring site</u>. As with the RK test, the NH is the slope of the change in concentrations over time is zero, while the AH is no change. The NH is rejected if the resulting p-value is ≤ 0.05 .

<u>Addressing Serial and Spatial Autocorrelation</u>. For each of the four tests, if their assumptions are violated, the resulting p-value can potentially be affected. If present, AC can adversely affect the assumption of independence (McHugh et al., 2011) and potentially lower the resulting p-value of the test (Dale and Fortin, 2002). For these reasons, both types of AC must be addressed. Regarding the WSR and MW tests, serial AC is accounted for because there are at least three years between each period. Spatial AC is not an issue for the WSR test because it is based on dependent matched pairs. The RK test accounts for both serial and spatial AC. The SK test accounts for serial AC and because each test addresses only one monitoring site, potential adverse effects caused by spatial AC are not an issue. The one remaining potential issue is spatial AC and the MW test. Later in this report (Gap Analysis), a discussion is presented that discusses how spatial AC in the network design was addressed. It will be demonstrated that spatial AC affects

wells up to approximately 14,373 ft. Because some of the wells are closer to each other than that distance, spatial AC likely affects the results of the MW tests. For this reason, discussions regarding the results of the MW tests should be taken with caution. Nevertheless, a discussion of the results of the MW tests sheds light on the changes in groundwater quality at each well.

TREND ANALYSES RESULTS

The results of the WSR tests are displayed in Tables 3. The table displays the results of the monitoring sites treated as a group. For each indicator, Table 3 addresses the question, "Did the water quality change between the Early and Late period in the Upper Floridan Aquifer (UFA) in Alachua County". The columns display the indicator, number of matched pairs (n), the resulting p-value of the test, if a trend was present, and the direction of the trend (slope). Significant trends are in **bold** font. The result of each WSR test, whether significant or not, is in Appendix C. The table indicates that from 1987 through 2021, concentrations of four indicators (Alk, Ca, K, and Na) increased.

Table 4 summarizes the results for each site displaying a trend, based on the MW test. For each indicator, the table displays the indicator, the corresponding p-value, and the direction of the trend if it was significant for individual monitoring sites. Only three sites displayed significant trends: wells AAE1420, AAE1421, and AAK7031. Because spatial AC among the wells may have resulted in the adverse lowering of the resulting p-values, the results need to be used with caution. The fact that trends (real or not) were observed at only three wells indicates that trends at individual monitoring sites were not common. For the three wells, the MW results suggest that concentrations increased in up to nine indicators (Alk, Ca, Cl, DO, K, Mg, Na, NO3, and SO4). In addition, downward trends were suggested in at least one well for DO and NO3. Test results for each site, whether listed as significant or not, are found in Appendix C.

Although not part of the trend analyses, it is interesting to note that for individual wells, NO3 was the only indicator that exceeded its drinking water health standard. Concentrations exceeded the standard in one well (AAJ3890) for each of the five times it was sampled.

Table 5 displays RK test results for all monitoring sites treated as a group. For the Late period and for each indicator, the table address the question, "Have concentrations changed in the Upper Floridan Aquifer in Alachua County for the period 2009-2021?" The table displays the indicator, the p-value, whether a trend is present, and the direction of the trend. Only indicators with trends are displayed. Results for all RK tests are found in Appendix C. During the Late period, concentrations of Ca and K increased, while the trend for DO was downward.

Regarding NH3, the RK test indicated the presence of a trend. However, upon further inspection, the trend is only an apparent trend, caused by changes in the laboratory method detection level (MDL). This topic will be discussed later.

Table 6 represents a summary of SK test results for 24 individual monitoring sites. The results for each SK test can be found in Appendix C. Table 6 displays the indicator, the total number of sites displaying trends, the number of increasing (upward) trends, and the number of decreasing (downward) trends.

| Indicator | Matched Pairs (n) | P-Value | Trend Present | Direction |
|-----------|-------------------|---------|---------------|-----------|
| Alk | 10 | 0.006 | Yes | Up |
| Ca | 10 | 0.006 | Yes | Up |
| Cl | 10 | 0.082 | | |
| DO | 10 | 0.387 | | |
| K | 10 | 0.048 | Yes | Up |
| Mg | 10 | 0.131 | | |
| Na | 10 | 0.005 | Yes | Up |
| NH3 | 10 | ISD* | | |
| NO3 | 10 | 0.351 | | |
| SO4 | 10 | 0.131 | | |
| TKN | 10 | ISD | | |
| TN | 10 | ISD | | |

Table 3. Results of Wilcoxon Signed Rank Tests for Sites as a Group Between the Early (1987-1999) and the Late (2009-2021) Periods. Significant trends are in **bold** font.

*ISD = Insufficient Data

 Table 4. Results of Mann-Whitney Tests for Individual Sites between the Early (1987-1999) and the Late (2009-2021) Periods. Only significant trends are displayed.

| Well | AAH | E 1420 | AAF | E 142 1 | AAF | K7031 |
|-----------|----------------|---------------|----------------|----------------|----------------|-----------|
| Indicator | P-Value | Direction | P-Value | Direction | P-Value | Direction |
| Alk | 0.002 | Up | < 0.001 | Up | | |
| Ca | < 0.001 | Up | < 0.001 | Up | 0.031 | Up |
| Cl | < 0.001 | Up | | | | |
| DO | 0.001 | Down | < 0.001 | Down | 0.029 | Up |
| K | 0.047 | Up | 0.004 | Up | | |
| Mg | < 0.001 | Up | < 0.001 | Up | 0.008 | Up |
| Na | 0.019 | Up | | | | |
| NH3 | | | | | | |
| NO3 | | | 0.034 | Down | 0.008 | Up |
| SO4 | < 0.001 | Up | 0.003 | Up | 0.002 | Up |
| TKN | | | | | | |
| TN | | | | | | |

One question that needs to be addressed is the rates at which the analyte concentrations changed. Estimates were derived both from the results of the WSR tests (Early to Late periods) and from the RK tests (Late period). Table 7 displays the estimated rates. Estimates are only presented for an indicator if there was a corresponding significant trend observed.

Regarding the WSR tests, estimated rates of change were calculated as follows. The median concentration from the Early period was subtracted from the median concentration in the Late period. For example, in mg/L, the median concentration of Ca for all samples in the E period was 67.75. In the Late period it was 75.50. The difference is 7.75. The middle year in the Early period (1987-2009) is 1993. The middle year in the Late period (2009-2021) is 2015. The difference between 2015 and 1993 is 22 years. Thus, the estimated rate of change for Ca is 7.75 mg/L divided by 22 years, or 0.35 mg/L/Yr. Regarding the RK tests, the estimated rates of

change are the Sen Slop estimate (Sen, 1968). The Sen slope estimates are read directly from the computer program output.

Table 5. Results of Regional-Kendall Tests for all Sites as a Group (2009-2021). Results represent overall changes in water quality in the Upper Floridan aquifer in Alachua County during the L period. Significant trends are in **bold** font.

| Indicator | P-Value | Trend Present | Direction of Trend |
|-----------|----------------|---------------|--------------------|
| Alk | 0.666 | | |
| Ca | 0.002 | Yes | UP |
| Cl | 0.261 | | |
| DO | 0.002 | Yes | Down |
| K | 0.016 | Yes | Up |
| Mg | 0.863 | | |
| Na | 0.570 | | |
| NH3 | 0.027* | | |
| NO3 | 0.857 | | |
| SO4 | 0.422 | | |
| TKN | 0.621 | | |
| TN | 0.404 | | |

*False positive trend

Table 6. Summary of Seasonal-Kendall Tests for Individual Monitoring Sites (2009-2021).

| Indicator | Number of | Number of | Number of |
|-----------|--------------------|-------------------|-------------------|
| | Significant Trends | Increasing Trends | Decreasing Trends |
| Alk | 4 | 3 | 1 |
| Ca | 9 | 9 | 0 |
| Cl | 8 | 4 | 4 |
| DO | 3 | 0 | 3 |
| K | 7 | 6 | 1 |
| Mg | 4 | 2 | 2 |
| Na | 10 | 6 | 4 |
| NH3 | NA* | NA | - |
| NO3 | 0 | 0 | 0 |
| SO4 | 9 | 6 | 6 |
| TKN | 1 | 0 | 1 |
| TN | 1 | 0 | 1 |

*NA: Not Applicable

Table 7 displays some interesting results. Concentrations of Alk, Ca, and Na increased for the duration of the investigation (1987-2021). During the Late (2009-2021) period, there were no observed changes for either Alk or Na. Alk, Ca and Na concentrations increased at 1.18, 0.35, and 0.11 mg/L/Yr, respectively, for the investigation duration. Rates of change occurring in the Late period were taken directly as Sen slopes (Sen, 1968) from the RK test output results (Appendix C). During the Late period, Ca increased by a rate of 0.67 mg/L/Yr. Regarding K, the rate of concentration change was <0.01 mg/L/Yr for both time periods. DO concentrations trended downward during the Late period (2009-2021) at a rate of -0.03 mg/L/Yr.

 Table 7. Estimated Rates of Change in Median Concentrations Based on Results of the WSR and RK Tests for Sites as a Group. Rates of change estimates were only reported if corresponding hypothesis test indicated the presence of a statistical trend.

| E (| 1987-1999) to L (20 (Step Trend) | · · · · · · · · · · · · · · · · · · · | L (2009 through 2021) (Time-Series Trend) | | |
|------------|-------------------------------------|---------------------------------------|--|-----------|-----------------------------|
| | | Estimated Rate (mg/L/Yr) | Indicator | Direction | Estimated Rate (mg/L/Yr) |
| Alk | Up | 1.18 | Alk | | |
| Ca | Up | 0.35 | Ca | Up | 0.67 |
| DO | | | DO | Down | -0.03 |
| K | Up | < 0.01 | K | Up | < 0.01 |
| Na | Up | 0.11 | | | |

PLAUSIBLE DRIVERS OF CHANGE

To assist in a discussion regarding the plausible causes of change the indicators were divided into indicator groups. Some indicators are classified into more than one group. Establishing cause and effect relationships are not part of this investigation. However, providing a list of plausible drivers of change is. Most of the plausible causes are modified from Upchurch (1992) and Upchurch et al, (2019). The indicator groups are displayed in Table 7. For detailed discussions regarding the origin of the indicators in natural water, see Hem (1985).

Table 8. Indicator Groups

| Group | Indicators |
|--------------------|-------------------|
| Nitrogen Nutrients | NH3, NO3, TKN, TN |
| Rock-Matrix | Alk, Ca, K, Mg |
| Salinity | Cl, K, Na, SO4 |
| Field | DO |

Nitrogen Nutrient Indicators

The indicators NH3, NO3, TKN, and TN fall into this group. Upchurch (1992) and Upchurch et al. (2019) indicated the sources of NH3 are often from decaying organics, fertilizers, animal waste, and industrial waste material. Increases in NH3 concentrations are likely related to increases in fertilizers and/or animal wastes. If NO3 is observed, the authors indicated the most likely sources are from fertilizers, plus animal, human, and industrial wastes, and possibly from recently increased atmospheric concentrations via rainfall. TKN is the sum of NH3 plus organic nitrogen. Sources are often from organics in swamps, wetlands, organic wastes, and from peat. TN reflects contributions of NH3, NO3, and organic nitrogen compounds. Significant changes in TKN and TN were not observed.

Upchurch et al. (2019 indicated that natural background concentrations of NO3 in Florida's groundwater is less than 0.05 mg/L. In addition, they stated that concentrations of NO3 have increased in Florida's groundwater for decades.

It should be noted that boxplots were generated using all available data from each period. This is different from the time-series plots that only used annual means and medians. The annual central tendencies were used to minimize effects of serial and spatial AC for trend analyses.

However, using all data for each period, the boxplots present a different perspective of changing water quality.

Figure 9 is a boxplot of NO3. The median NO3 values for each period are 0.85, 1.10, and 1.10 mg/L, respectively. Note, based on the statistical tests, there is no evidence of an upward trend. However, the median concentration value increased between the Early and Middle periods but did not change between the median and Late periods. The leveling is welcome news. Ideally, it is related to a net decrease in the amount of nitrogen waste material and/or fertilizers finding their way to land surface, and subsequently to the UFA. Unfortunately, it is beyond the scope of this study to quantify the loadings to the UFA.

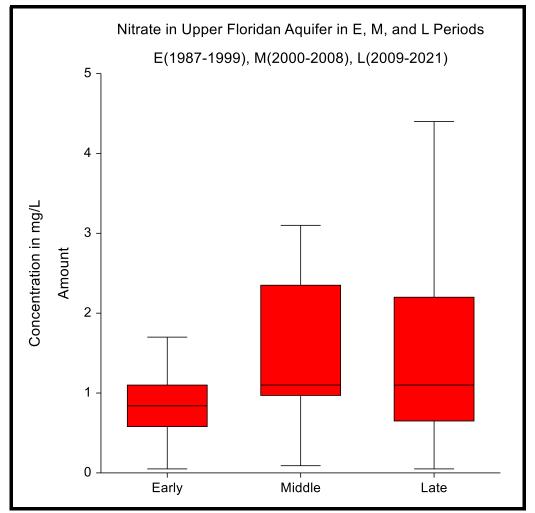


Figure 9. Boxplots of Early, Middle, and Late data for Nitrate.

Again, referring to the works of Upchurch (1992) and Upchurch et al (2019), causes of change in NO3 concentrations are complex. The authors mentioned a list of potential drivers, including oxidation/reduction, DO, the ratio of NO3 to ammonium (NH4), water temperature, and biological activities.

Increasing groundwater levels is another potential driver. Precipitation (rainfall) and recharge increased during the Late period. (Precipitation increases will be discussed later.) Gao et al. (2012) stated that in unconfined aquifers during periods of increased rainfall and net recharge, NO3 can be flushed from the soil and migrate into underlying aquifers. This will result in increased NO3 concentrations. However, during the Late period, nitrogen concentrations appear to have leveled off. A potential explanation is that after a sufficiently long period of increased rainfall, after a lag in which the nitrogen is mostly flushed out, NO3 concentrations can level off and even decrease because of dilution within the aquifer.

Table 4 suggests that during the Late period, NH3 concentrations increased. However, an inspection of the Late period time-series plot of annual median concentrations (Figure 10) revealed a problem. In units of mg/L, for the years 2015-2019 (five years) almost all NH3 concentrations were reported as 1.00. In fact, between February 2015 and August 2019, NH3 concentrations in 115 consecutive samples were reported as 1.00, and the corresponding annual means and annual medians were calculated as 1.00. Upon inspection, instead of these values representing NH3 concentrations in the aquifer, each of the individual values represents the laboratory method detection level (MDL). The concentrations reported as 1.00 were likely to be less than or equal to the 1.00 MDL. These reported values biased the trend analyses results. The increasing trend was false. The actual NH3 concentrations, labeled as 1.00 for that period are not known.

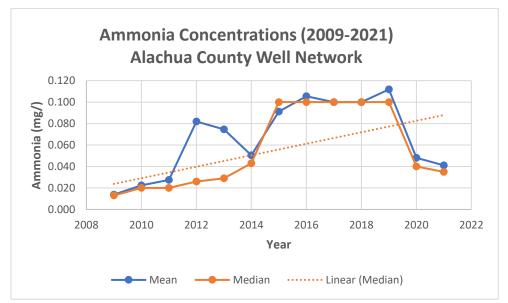


Figure 10. Annual NH3 Mean and Median Concentration (2009-2021).

Rock-Matrix Indicators

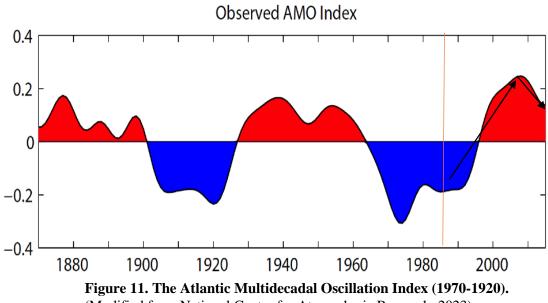
These indicators include Alk, Ca, K, Mg, and SO4. Carbonate (CO3) in the form of bicarbonate alkalinity (Alk), Ca, and Mg make up the matrix material of the dolostones and limestones of the Upper Floridan aquifer (UFA). Dissolution of matrix material in the UFA contributes to increased concentrations of these analytes in its groundwater. Sources of K in groundwater can be from seawater, connate water, potassium-rich clays overlying the UFA, fertilizers, and disposal of waste material. Connate water is the sea water trapped in the pore spaces of the carbonate material during original deposition. A source of SO4 in the UFA

groundwater is from the dissolution of gypsum and anhydrite in the middle confining unit separating the UFA from the Lower Floridan aquifer. Other sources of SO4 are from seawater, connate water, peat, and pyrite. Pyrite occurs in the Hawthorn Group (Scott 2016), which overlies the eastern portion of Alachua County.

Salinity Indicators

Indicators in this group are Cl, K, Na, and SO4. Sources of all four indicators include seawater and connate water. Other sources of Na are from clay material and from waste material. As mentioned before, sources of K are from clay material, fertilizers, and disposal wastes. Other potential sources of SO4 are from peat and industrial wastes.

To better understand the plausible changes in Rock-Matrix and Salinity indicator concentrations, a conceptual model was developed by Copeland and Woeber (2021) and Copeland et al. (2023), In two statewide investigations of the Florida Aquifer System (FAS), including the UFA, the authors found that for the period (1991-2020), a correlation exists between the amount of rainfall and the concentrations of Rock-Matrix and Salinity indicators, such as Alk, Ca, K, Mg, SO4, Na, and Cl. As rainfall decreased, concentrations of these indicators increased throughout Florida. Beginning in the late 2000s, rainfall began to increase, and after a lag, the concentrations of these indicators began to decrease. The authors also found a correlation exists between the Atlantic Mutidecadal Oscillation (AMO) Index (National Center for Atmospheric Research, 2023) and concentrations for these indicators. The AMO Index is related to the sea surface temperatures of the North Atlantic Ocean. Figure 11 is a modified plot of the AMO Index by year from 1870 through 2020 (National Center for Atmospheric Research, 2023). The yellow vertical line in 1987 was added by the authors. It represents the initial sampling of the ACEPD groundwater monitoring network. The first black arrow (added by the authors) displays an increasing AMO Index value from 1987 through the late 2000s. The second black arrow (also added by the authors) displays the most recent decreasing AMO Index. Figure 12 displays annual mean precipitation from the Gainesville Airport, in inches per year, for the period 1987-2021. Note that rainfall decreased between 1987 through the late 2000s. However, it then increased through 2021. Figure 13 displays mean annual Florida precipitation for the period 1991 through 2019. Data are from the Florida Climate Center (2023), while the figure is from Copeland and Woeber (2021). Again, note that rainfall decreased from the early 1990s and then increased through the late 2010s. Also note the inverse correlation of the rainfall with the AMO Index.



(Modified from National Center for Atmospheric Research, 2023)

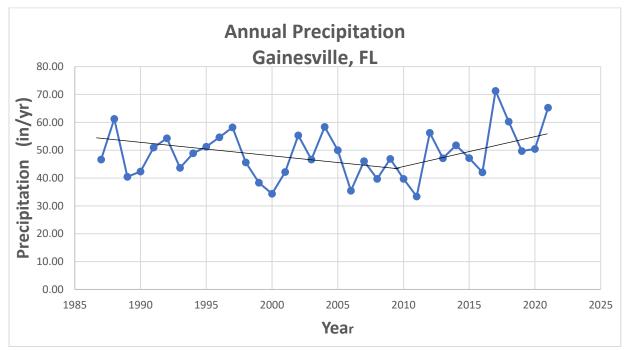


Figure 12. Gainesville Precipitation by Year (1987-2021). (Florida Climate Center, 2023)

A conceptual model regarding the thickness of the freshwater portions of Florida's groundwater to: (1) concentration changes of Rock-Matrix/Salinity Indicators to (2) rainfall is displayed in Figure 14. It is based on the Ghyben-Herzberg relationship (Freeze and Cherry, 1979). A description of the model is an abridged version taken from Copeland et al. (2021),

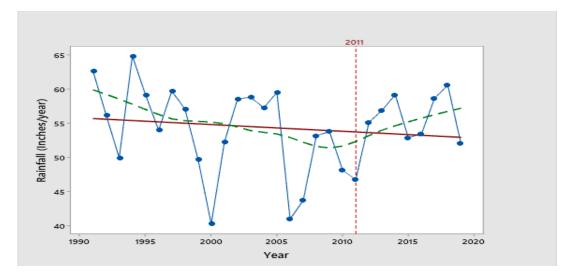


Figure 13. Florida Statewide Precipitation by Year (1991-2019). (From Copeland and Woeber, 2021)

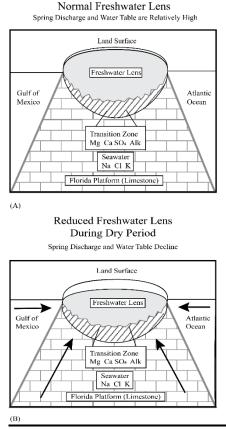


Figure 14. Relationship of thickness of Freshwater Lens of groundwater in Florida to Concentration changes of Rock-Matrix and Salinity Indicators (Copeland and Woeber, 221).

Freeze and Cherry (1979) indicated that in the ideal Ghyben-Herzberg relationship, for each meter of drawdown the saltwater/freshwater interface, in an ideal coastal aquifer, rises by 40 meters as a sharp line. In Figure 14, all of Florida's freshwater aquifers and confining units are conceptually lumped together into a freshwater lens. The irregularly shaped lens is generally thickest in the central portion of the state and narrows toward Florida's coastlines. The top part of Figure 14 represents the lens during normal rainfall times. Notice the thickness of the freshwater lens. The bottom part of the figure represents the lens after long periods of below-normal rainfall. Notice the thickness of the lens. It has decreased in size. In addition, the upper surface of the lens has been lowered. In the Floridan Aquifer System, deep groundwater is enriched in carbonate rock-matrix indicators such as Ca, Mg, K, Alk, and SO4, along with both Na and Cl (Upchurch et al. 2019; and Sprinkle, 1989). During periods of extended below-normal rainfall, the deep enriched groundwater can potentially migrate inland horizontally from the edges of the lens, upward vertically from the transition zone, and into the UFA.

Krause and Randolph (1989), and Spechler (1994) hypothesized that deep relict sea water may be a major source for increased saline indicator concentrations in portions of the FAS in northeastern Florida. The authors stated the deep water provides the major source of Na, Cl, K, Mg, and SO4. Berndt et al. (2005) indicated that spring discharge water can originate from both shallow and deep sources. Although not displayed in Figure 14, it is implied that if a period of above-normal rainfall prevails and if recharge exceeds discharge for a long enough time, the lens will increase in size and concentrations of Na, Cl, and rock-matrix indicators will eventually decline.

Figures 11-13 suggest an inverse relationship between the AMO and Florida precipitation. The figures, plus Tables 2-6 display an inverse relationship between (1) rainfall in both Alachua County and Florida and (2) concentrations of the Rock-Matrix and Saline indicators. They also support the conceptual model depicted in Figure 14.

Field Indicator

The lone field indicator in this investigation is DO. During the Late period, its concentration decreased (Tale 6). Upchurch (1992) mentioned that concentrations of DO in water are dependent on temperature and atmospheric pressure. The U.S. Geological Survey (USGS) (2023) indicated that as temperature increases, DO concentrations can potentially decrease in groundwater and surface water.

During the Late period, air temperature across Florida increased (Florida Climate Center, 2023). Based on data from a statewide water quality database at the Florida Department of Environmental Protection (the Generalized Water Information System), the authors found that groundwater temperatures in unconfined aquifers throughout Florida also increased. Thus, evidence suggests that increasing groundwater temperatures are the driving force of decreasing DO concentrations. However, other potential drivers exist. Upchurch (1992) mentioned that biota can consume oxygen as they travel along groundwater flow paths, resulting in a lowering of DO concentrations.

GAP ANALYSIS

Purpose

The purpose of this exercise was to find locations where additional network wells are needed. ACEPD sought to determine the distance at which spatial autocorrelation was

considerably reduced between well measurements. Determining the variation in indicator readings spatially informs ACEPD to the ideal coverage of monitoring wells needed. The final result was a map of hexagons.

Gap Analysis Methods

ACEPD performed a gap analysis using chloride as a trace element. Chloride provides a good basis for this analysis as it is neither involved in major precipitation nor dissolution reactions under the conditions found in Florida's aquifer system (Boniol and Toth, 1999). Chloride between 2013 and 2023 were compiled from Suwannee River Water Management District (SRWMD), St. Johns Water Management District (SJWMD), and FDEP within a search box surrounding Alachua County. The data were examined and cleaned up to generate one uniform latitude and longitude unit for further processing in the statistical package R, and ArcGIS Pro. ACEPD removed outlier data from a monitoring well at the Gainesville Regional Utilities Kanapaha Wastewater Treatment Plant.

Wells used for the kriging analysis were selected using a ten-mile buffer around Alachua County. Mean chloride concentrations were calculated when multiple measurements were recorded per station. The data was then analyzed with the Geostatistical Analysis Extension. In the Geostatistical Analyst Extension, Ordinary Kriging Prediction Method with Exponential Model was used.

The semivariogram was examined using the Geostatistical Kriging Wizard (Figure 15). The semivariogram assesses the variability between two random variables as distance between variables increases. The distance where the semivariogram model levels out is known as the range. Distances closer than the range are spatially autocorrelated, while those locations farther apart are not autocorrelated. The range determined from this dataset was 14,373 feet.

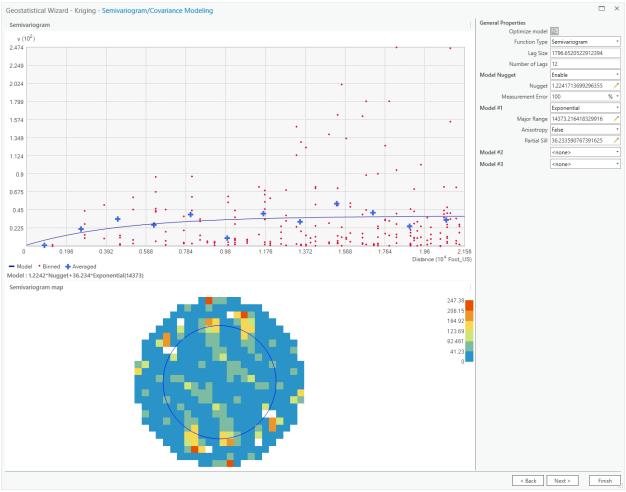


Figure 15 Semivariogram Readout from ArcGIS Pro.

ACEPD created hexagon maps to compare standard deviations (sd) as the size of hexagons increased. Previous network design completed by the St Johns Water Management District used a hexagonal spacing for sampling selection based on findings that a hexagonal sampling pattern produces both the lowest average and maximum standard errors (Olea et. al 1984). Using the geoprocessing tool, Generate Tessellation, the authors created hexagons of differing sized diameters of 15,000 ft, 20,000 ft, 30,000 ft, 40,000 ft, and 50,000 ft (Figure16 a, b, c, and d).

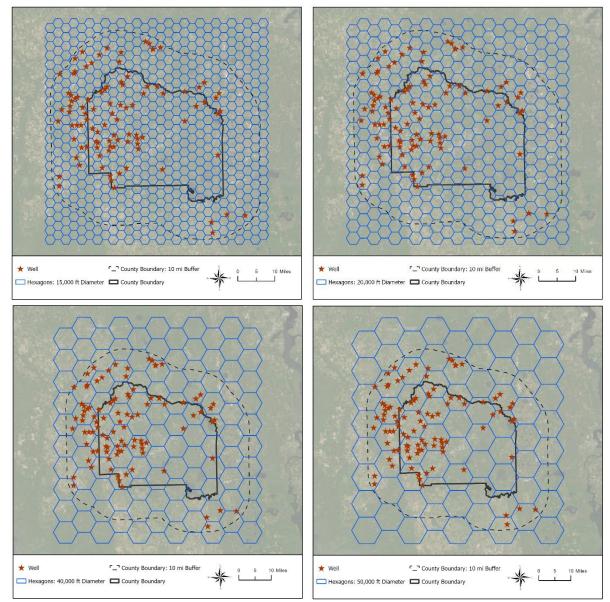


Figure 16 a-d. Well Sample Points from ACEPD, SRWMD, SJWMD and Hexagonal Tessellation Overlay in Alachua County with Diameters of 15,000, 20,000, 40,000 and 50,000 feet.

Wells that fell within the same hexagon were binned together to calculate the corresponding sd using the Summary Statistic Tool in ArcGIS Pro (Figure 15). Standard deviation increased as hexagon area increased. ACEPD used the sd graphs as a secondary evaluation of spatial autocorrelation.

Gap Analysis Results

The geostatistical analysis of the summarized chloride data concluded that the ideal placement of wells within a monitoring network should be greater than 14,373 feet. ACEPD used this range to examine what a monitoring well network might look like with one well per hexagon. Hexagon grid configuration varied in size and included 15,000 ft; 20,000 ft; 30,000 ft;

40,000 ft; and 50,000-ft diameters. The 15,000 ft diameter tessellation was the closest distance to the range identified in the semiovariogram. Including a well point in every hexagon that had its center located within Alachua County at the 15,000 ft diameter would require a network of 188 wells. Due to the limits on budget and time this high a resolution of wells is not practical. Comparatively, a well network with hexagon diameters of 20,000 is 160 wells, for 30,000 ft diameters it is 45 wells, for 40,000 ft diameters 28 wells, and for 50,000 ft diameters 16 wells.

Limitations for well monitoring include both time and budget. The current network of monitoring wells includes 18 stations, mostly situated in the western portion of Alachua County where the aquifer is unconfined (Figure 3). Overlaying the well network with the 30,000-foot diameter hexagons would be a good starting point for selecting additional locations (Figure 17). Alachua County should focus future selection of well stations in hexagons without sample stations that fall within the unconfined and semi-confined zones with highest priority then move to unrepresented hexagons in confined portions of eastern Alachua County. Using the 30,000 ft hexagon grid there are five hexagons in the unconfined zone, and 18 hexagons in the confined portion of the County (Figure 17). ACEPD should prioritize sample locations within the unconfined portion of the County first, before moving to the perforated region, and finally the confined portion of the County.

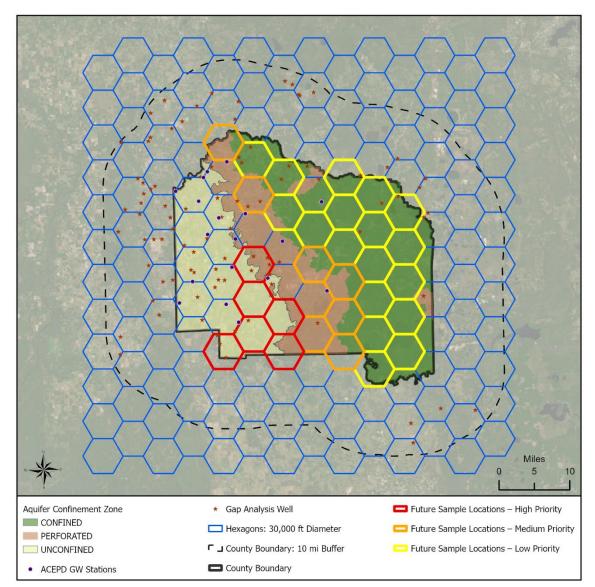


Figure. 17 Location of ACEPD Groundwater Stations, and prioritization of new sample locations needed within the County using a 30,000 ft diameter hexagon.

RECOMMENDATIONS

The author has four recommendations for the ACEPD. The intent was to address key issues but to also minimize additional costs. The recommendations are:

- 1. Add wells to the network as needed to fill in geographical gaps in the network.
- 2. Continue to monitor both in the dry and in the wet seasons.
- 3. Insist on using the lowest laboratory Method Detection Level (MDL) possible for nutrient indicators.

4. When reporting indicator values, include corresponding laboratory MDLs.

The ACEPD has conducted a gap analysis exercise. The purpose was to find locations where additional network wells are needed. The result was a map of hexagons. The "empty" gaps (hexagons lacking monitoring sites). Filling in the gaps results in an increased ability of the ACEPD to detect changes in groundwater quality. This is because filling in the gaps reduces the adverse effect of spatial autocorrelation.

The ACEPD has monitored the UFA during the Wet and in the Dry seasons for over a decade. Continue to monitor in both seasons and minimize seasons of no sampling. Whereas adding sampling sites in gaps reduces adverse effect of spatial autocorrelation, filling in the seasonal time gaps reduces adverse effects of serial autocorrelation.

ACEPD should insist that analytical laboratories use the lowest MDL. For indicators that typically have concentrations significantly greater than the MDL, this is usually not an issue. However, for indicators that often have high MDLs, relative to aquifer concentrations, this is especially important. This situation is often encountered for nutrient data. A recommendation of using an MDL of 0.04 mg/L or lower for NH3, NO3, TKN, and TN is recommended. Using the appropriate MDLs reduces the potential to calculate false trends, such as occurred for NH3 during the L period.

During this project, the author observed that some concentration values were reported as 0.00 mg/L. For the network indicators, a value of 0.00 is not possible. Instead, report the corresponding MDL. Statistical procedures are available for trend analysis that address MDLs. In addition, it is possible that a future analyst will interpret the 0.00 values as a missing value, which is not true.

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APPENDICES

All Appendices are in Separate Excel Files.

APPENDIX A. DATA

Appendix A1. ACEPD Data Appendix A2. Data by Indicator with Means and Medians Appendix A3. Data by Well Appendix A4. Data for MW Tests Appendix A5. WSR Test Data Appendix A6. Gainesville Airport Precipitation by Year

APPENDIX B. TIME-SERIES PLOTS AND BOXPLOTS

Appendix B1. Time-Series Graphs Appendix B2. Boxplots

APPENDIX C. STATISTICAL TEST RESULTS

Appendix C1. Individual Well MW Test Results Appendix C2. Individual Well SK Test Results Appendix C3. RK Test by Group Results Appendix C4. WSR Test by Group Results