Four-Year Progress Report, January 2013–December 2016

Implementation of Best Management Practices in the Santa Fe Restoration Focus Area:

Nitrate-N Concentrations in Groundwater, Springs, and River Water

A Joint Document Prepared by the

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Executive Summary

As part of the basin management action plan (BMAP) to restore water quality in the Santa Fe River and its impaired spring-fed tributaries by reducing nitrogen loads to the system, the Florida Department of Environmental Protection (DEP) and the Florida Department of Agriculture and Consumer Services (FDACS) Office of Agricultural Water Policy (OAWP) are collaborating on a restoration focus area (RFA) in the Santa Fe River Basin. The 185-square-mile RFA includes the combined springsheds of Ginnie and Gilchrist Blue Springs, a significant source of nitrate-nitrogen to the lower Santa Fe River. Major land use/land cover (as of 2010) in the RFA includes forestland (44 %), agriculture (29 %), and urban/residential (12 %; mostly low-density residential).

Within the RFA, agency resources are focused on working with agricultural producers to implement nutrient management best management practices (BMPs) and on monitoring associated water quality changes in groundwater, springs, and the Santa Fe River. The RFA activities began in January 2013 and include ongoing OAWP efforts to maximize enrollment in agricultural BMPs for vegetable and agronomic crops and cow-calf operations, and DEP efforts to monitor water quality at 20 monitoring wells, 4 springs, and 3 Santa Fe River stations.

In addition, continuous water quality monitoring equipment (nitrate as nitrogen [nitrate-N], pH, temperature, dissolved oxygen, and specific conductance), a rain gauge, and a velocity meter were installed at Ginnie Springs to better understand how nitrate-N in water from the spring responds to rainfall, fluctuations in groundwater levels, land use practices, and other factors.

Progress and findings from the initial four years of RFA activities (January 2013–December 2016) include the following:

- The OAWP worked with landowners and producers to enroll most of the large tracts of commercial agricultural acreage in its BMP programs. The number of notices of intent (NOIs) signed by landowners to implement BMPs on agricultural properties in the RFA increased from 135 at the end of December 2015 to 150 at the end of December 2016. Landowners have committed to implement BMPs on a total of 34,369 acres of agricultural lands in the RFA.

- The main source of elevated nitrate-N concentrations in groundwater and spring water is inorganic fertilizer, based on chemical data for nitrate isotopes, potassium, chloride, and bromide. There was a statistically significant ($p<0.05$) correlation between nitrate-N and potassium concentrations in wells near irrigated sites. In contrast, at nonirrigated sites there was a statistically significant inverse correlation between nitrate-N and potassium concentrations.

- Thirteen monitoring wells are located adjacent to and/or downgradient from agricultural parcels where BMPs are being implemented or where a commitment to implement BMPs has been received (in the form of a signed NOI). Nitrate-N concentrations in quarterly samples from these wells were assessed for trends over the 4 years of the study using nonparametric statistical tests. Five of the 13 wells had statistically significant increasing trends, 4 had decreasing trends, and 4 showed no trend over time. Nitrate-N concentrations decreased substantially

(from 25 to 4.5 milligrams per liter [mg/L] and 10 to 5.3 mg/L) between January 2013 and September 2016 in 2 wells. Both are located near irrigated field crops and pasture that support a dairy or former dairy. One property was enrolled in BMPs after monitoring started. The OAWP is currently gathering more detailed information about the timing and specific types of BMPs being used at agricultural sites near the monitoring wells.

- No trends in nitrate-N concentrations were observed over time for wells located near or downgradient from residential areas or the Newberry wastewater treatment facility.

- No significant decreases in nitrate-N concentration were observed over the four-year period in the sampled springs or Santa Fe River sites. This lack of response may be related to (1) insufficient time for changes in agricultural practices to affect groundwater quality (a lag effect between when BMPs are implemented and when improvements in water quality are seen); (2) legacy nitrogen in soil and shallow groundwater from past practices; (3) possible compliance issues in the implementation of BMPs (although BMP compliance will be verified with implementation assurance visits by the OAWP); and/or (4) the limitations of BMP effectiveness because of soil conditions, cropping rates, fertilization rates, and irrigation needs that may warrant additional measures (if water quality problems are observed despite BMP implementation).

Introduction

As part of the basin management action plan (BMAP) to address nutrient total maximum daily loads (TMDLs) in the Suwannee River Basin, the Florida Department of Environmental Protection (DEP) and the Florida Department of Agriculture and Consumer Services (FDACS) Office of Agricultural Water Policy (OAWP) selected a restoration focus area (RFA) in the Santa Fe Springs Basin. The purpose of an RFA is to concentrate staff and funding on expediting the implementation of best management practices (BMPs) and evaluating their impact on water quality. The Ginnie and Gilchrist Blue springsheds were selected to evaluate how BMPs affect nitrogen loading to groundwater and nitrate as nitrogen (nitrate-N) concentrations in springs.

The Santa Fe Basin RFA shown in **Figure 1** was delineated using springshed maps from a groundwater flow model developed by Geohydros (Kinkaid et al. 2009). The RFA is bounded to the north by the Santa Fe River, to the east by the Poe and Lily Springs springsheds, to the west by the edge of the Waccasassa Flats, and to the south by the southern edge of the Santa Fe River groundwater contributing area. It is based primarily on a composite of modeled low-flow (worst-case) groundwater capture areas (springsheds) for Ginnie and Gilchrist Blue Springs, but the RFA also includes the smaller Twin Spring springshed to the west, a small area between the Ginnie-Gilchrist Blue and Poe-Lily springsheds, and the major springs that discharge into the Santa Fe River west of Poe Spring from south of the river. In addition, the RFA includes the groundwater contributing area of the Devil's Complex, which includes vents of Devil's Eye and Devil's Ear Springs. The criteria for selecting this area are listed in the joint document, *Focused Implementation of Best Management Practices in the Santa Fe River Basin* (DEP-FDACS 2013).

The RFA covers an area of 185 square miles in Gilchrist and Alachua Counties. According to the most recent land use/land cover map of the Suwannee River Water Management District (SRWMD), based on 2013 information, the major land uses/land cover in the area include forestland (42 %), agriculture (31 %), urban/residential (12 %, mostly low-density residential), wetlands (6.9 %), upland nonforested (5.1 %), and transportation and barren lands (2.5 %). A ground-truthed land use map for the RFA developed in 2012 (**Figure 2)** highlights land uses that may contribute nitrate-N to groundwater. This joint DEP-FDACS effort is monitoring and documenting land use changes in the RFA that may influence nitrogen loading.

The City of Newberry, the only incorporated area in the RFA, covers 54.6 square miles. Newberry has its own wastewater treatment facility (WWTF), which serves the more densely developed portion of the city and has a design flow of 0.499 million gallons per day (mgd). This WWTF discharges treated effluent to a spray field in the RFA. Septic systems, also referred to as onsite sewage treatment and disposal systems (OSTDS), serve the remaining homes and businesses in the RFA. Overall, there are 3,500 OSTDS in the Santa Fe Basin RFA, most of them in the Newberry area. Also, the High Springs WWTF in Alachua County lies just outside (east and upstream of) the RFA boundary and has a design capacity of 0.24 mgd.

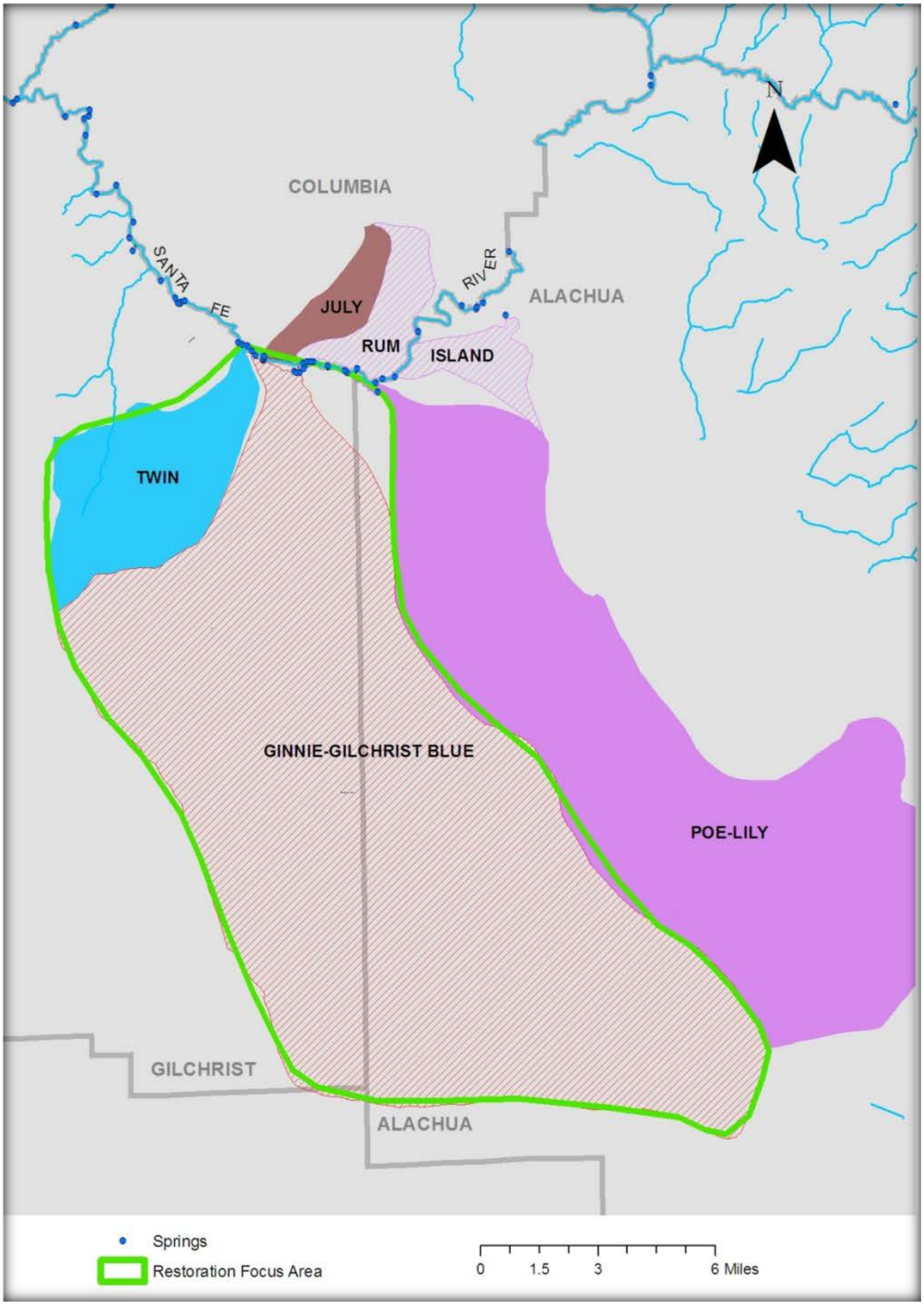

Figure 1. **Santa Fe Springs Basin, RFA boundary, and adjacent springsheds**

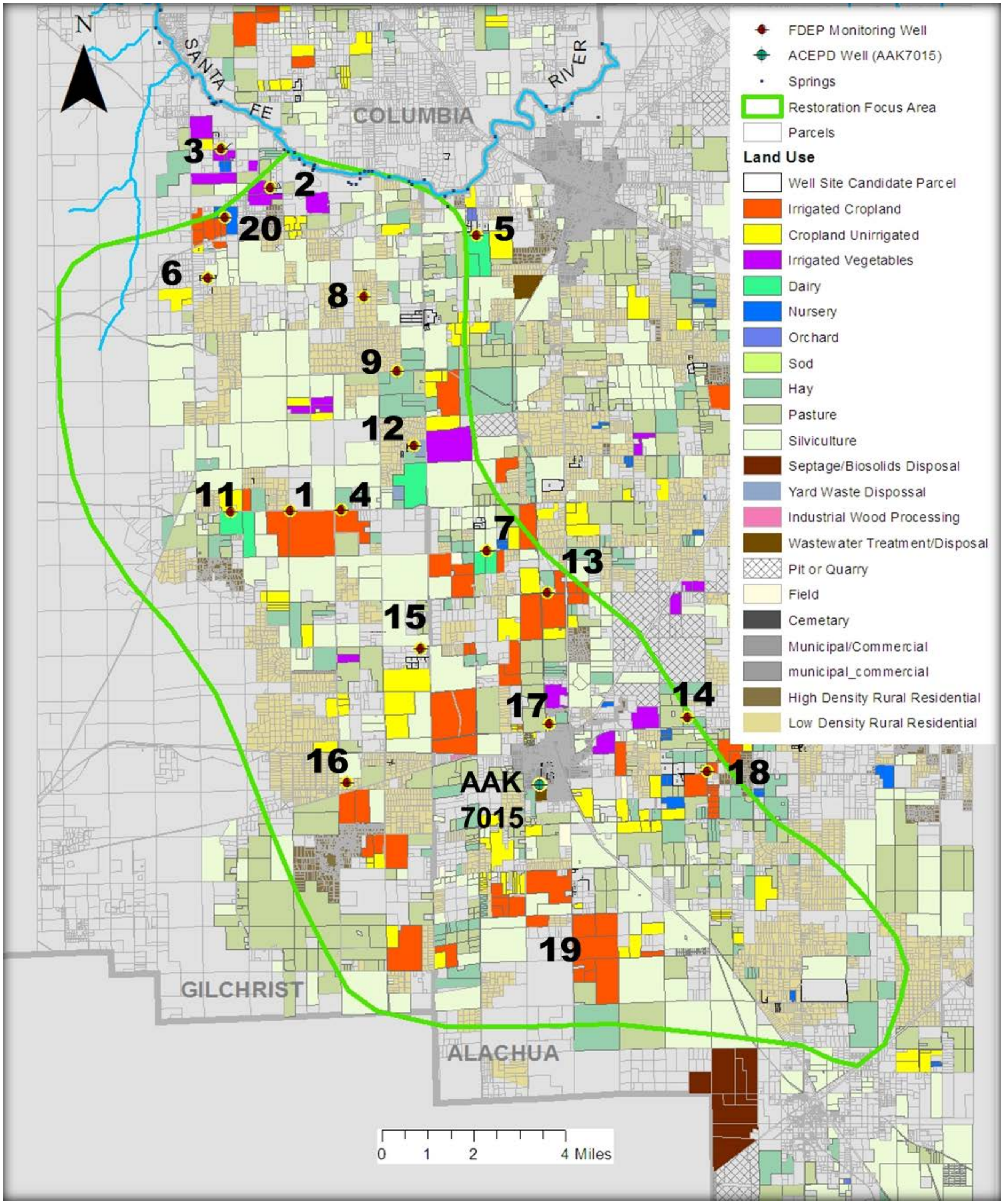

Figure 2. **Land use and monitoring well locations in the Santa Fe Basin RFA in 2012**

The strategy for evaluating the water quality effects of BMPs and other actions in the RFA includes two main components of measurement: (1) quarterly water quality monitoring of groundwater, springs, and river water; and (2) enrollment in and the implementation of BMPs for cow-calf operations, container nurseries, vegetable and agronomic crops, and dairies (FDACS 2008a, 2014, 2015, and 2016, respectively). This second component includes gaining agricultural landowner participation in the FDACS BMP Program, identifying priority practices to focus cost-share and implementation assurance efforts (nutrient, irrigation, and water resource protection BMPs), and determining compliance with applicable fertilizer ordinances in urban areas. Also, the FDACS Forest Hydrology Section's 2008 *Silviculture Best Management Practices Manual* provides information to Florida's private and public forest landowners on BMPs associated with silviculture activities.

The DEP–FDACS annual progress report (2014) describes the RFA process, criteria for selecting the RFA, actions completed to attain stakeholder involvement in the RFA effort, steps for assessing progress in the RFA, and the water quality monitoring plan. DEP and FDACS also prepared a three-year (2013–15) progress report (published in 2016) that includes water quality and BMP enrollment information collected from 2013 through 2015.

This four-year progress report includes comprehensive information collected from January 2013 through December 2016. The water quality information presented here focuses on nitrate-N concentrations in groundwater, springs, and river water samples. However, other chemical data are included that help to determine the sources of nitrate and processes that affect the movement of nitrate in the RFA.

Water Quality Monitoring Network

Groundwater Sites

Table 1 lists the 20 monitoring wells that were installed, developed, and surveyed for the groundwater monitoring network in the RFA. In addition, a monitoring well near the Newberry WWTF spray field was added to the sampling network in August 2013. **Figure 2** shows the locations of the groundwater monitoring wells in relation to land use and land cover designations in the RFA. Water samples were collected quarterly from the monitoring wells during 2013 and 2014. In 2015, DEP sampled the wells during March, June, and September. In 2016, it sampled the wells in March and September, except for Monitoring Well (MW) 12, which was sampled in March, June, September, and December.

Selected groundwater quality data (nitrate-N, potassium, sulfate, and dissolved solids) and groundwater levels for the period from January 2013 to July 2016 were evaluated using statistical tests for trends and seasonality (R. Copeland, 2016, DEP, written communication). Seasonality tests were conducted for quarterly and semiannual sampling. Based on the groundwater level data, a dry season runs from November through April, and a wetter season typically extends from May through October. However, wet and dry seasons can vary, and in some years, the wet season is January–March and June–August, and the dry season is April–May and September–December. A statistically significant six-month seasonality was found for groundwater levels. However, nitrate-N, potassium, sulfate, and dissolved solids did not show statistically significant seasonality.

Based on the results from the seasonality tests for nitrate-N, potassium, sulfate, and dissolved solids, the sampling schedule was modified after September 2015. The revised sampling frequency of the monitoring wells included a reduction from quarterly to semiannually, except for MW12, where water samples indicated high nitrate-N concentrations (greater than 40 milligrams per liter [mg/L]) and an increasing trend during the study period. This site is also located near a groundwater remediation system that recovers groundwater in an area of high nitrate concentration, treats it in a bioreactor to reduce nitrate levels, and returns it to the aquifer.

Table 1. Summary information on monitoring wells used in the RFA pilot study

[1] Used in Alachua County Environmental Protection Division quarterly monitoring program.
[2] Information in comments is from December 2012 field observations and other data. These are updated as new information is received.
N/A = Not available

Monitoring Well Number	Well Screen Interval Depth (feet)	Adjacent Land Use	Well Distance from Land Use (feet)	Comments[2]
MW1	38–48	Irrigated cropland	40	In production since 2012; previously scrub
MW2	38–48	Irrigated vegetables	30	In production since 2012; previously pasture
MW3	21–31	Irrigated vegetables	430	Vegetables since 2004 aerial; pasture before that
MW4	58–68	Irrigated cropland	40	Partially irrigated cropland since before 1994
MW5	48–58	Pasture/crop; supporting dairy	75	Dairy since before 1994 (current status unknown)
MW6	25-–35	Low-density residential		Potential septic tank influence
MW7	48–58	Irrigated field crop supporting dairy	20	Dairy since before 1994 (current status unknown)
MW8	58–68	Low-density residential	N/A	Background
MW9	44–54	Pasture	90	Pasture or nonirrigated crops 20+ years
MW10	61–71	Irrigated cropland	100	Irrigated cropland since before 1994
MW11	38–48	Irrigated field crop and pasture supporting dairy	40	Dairy since before 1994
MW12	68-78	Residential, irrigated field crop supporting dairy	35	Dairy since early 2000s; residential developed in early 2000s
MW13	51–61	Irrigated cropland	90	Was pasture until 2010
MW14	48–58	Hay	20	Hayfield or pasture since before 1994
MW15	61–71	Irrigated cropland	2,300	Multiple agricultural land uses in vicinity
MW16	58–68	Irrigated cropland	60	No change in land use since before 1994
MW17	35–45	Urban	N/A	In Newberry urban area
MW18	55–65	Irrigated cropland	80	Cropland since before 1994; irrigated since 2000
MW20	58–68	Irrigated cropland	360	20+ years; irrigated in early 2000s
AAK7015[1]		Domestic wastewater spray field and cemetery		Adjacent to City of Newberry WWTP spray field

Springs and Surface Waters

DEP collected quarterly spring water quality samples from Ginnie Spring, Gilchrist Blue Spring, Devil's Eye Spring, and Twin Spring (**Figure 3**) from 2013 to 2016. These represent the major spring discharges to the Santa Fe River in the RFA. DEP also collected river water samples quarterly at three stations on the Santa Fe River from 2013 to 2016 (**Figure 3**). **Figure 8** shows the mean daily discharge values for the Santa Fe River at Fort White for this period.

Continuous Monitoring at Ginnie Spring

Specialized continuous monitoring equipment was installed in March and April 2014 at Ginnie Spring to obtain continuous measurements of nitrate-N and other water quality parameters. Continuous water quality sensors include probes to measure pH, temperature, dissolved oxygen (DO), and specific conductance (SC). A submersible ultraviolet nitrate analyzer (SUNA) provides measurements of nitrate (as nitrogen). Also, a rain gauge installed near Ginnie Spring provides continuous measurements of rainfall. In addition, equipment was installed in the spring to continuously measure spring stage, velocity, and flow direction. Spring flow (discharge) is estimated by multiplying the water velocity times the cross-sectional area of the spring vent opening.

Water from the spring is pumped 80 feet to a flow-through cell housed in a nearby shelter, where the various sensors take periodic measurements. The nitrate-N and other water quality data are analyzed relative to information on rainfall, groundwater levels, spring flow, river flow, and other factors.

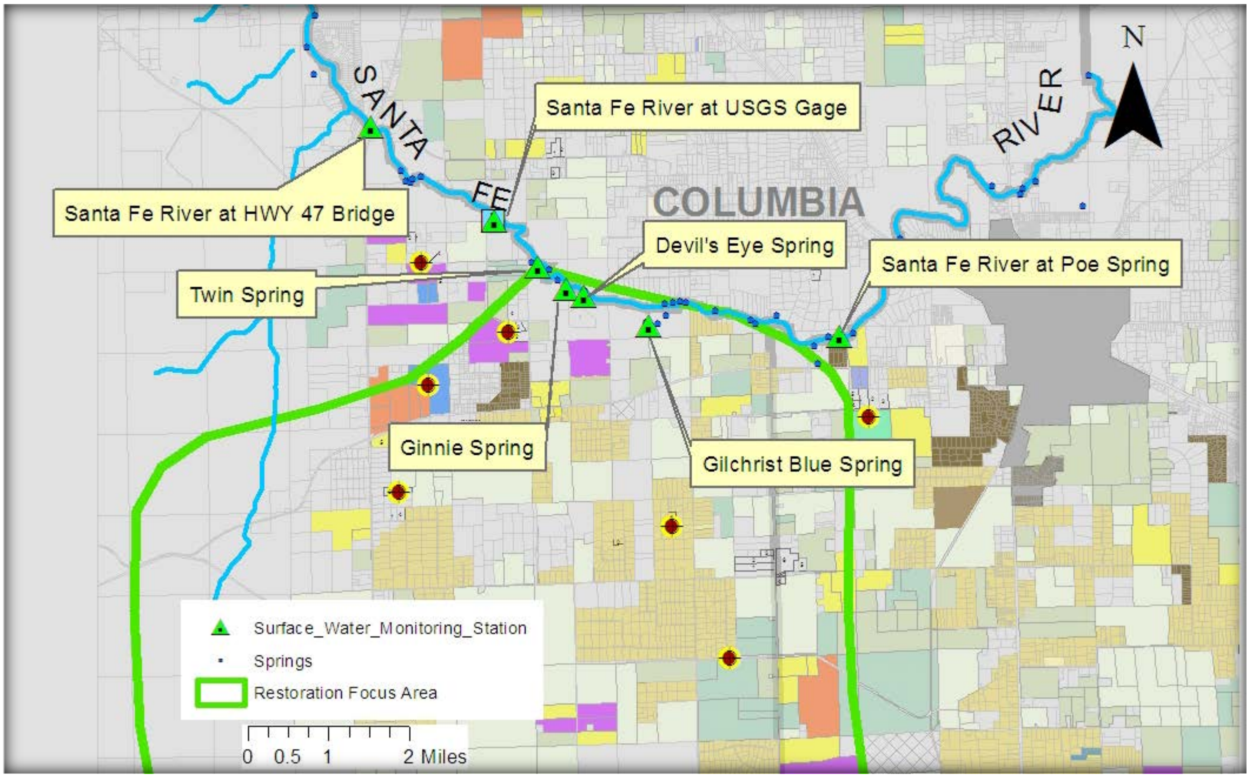

Figure 3. Santa Fe River Basin RFA springs and river monitoring stations

Results

Nitrate-N Concentrations in Groundwater, Spring Waters, and River Water

One of the main objectives of the RFA study is to investigate the transport and fate of nitrate-N in groundwater, springs, and surface water. Another important objective is to evaluate the relationships between changes in nitrate-N concentrations in wells, springs, and river sites with the increased implementation of BMPs in the RFA. Therefore, this section focuses primarily on nitrate-N measured in the groundwater, springs, and river water samples collected during the first four years of the study (2013–16). **Appendix 3** lists the complete set of water quality results from groundwater, springs, and river samples collected from 2013 to 2016, along with analytical data qualifiers and quality assurance/quality control (QA/QC) information.

Groundwater

Monitoring wells were subdivided into 4 groups based on similar land use classification for the sake of comparing nitrate-N concentrations (pastures supporting dairies, irrigated cropland, hayfield and nonirrigated pastures, and residential and WWTF spray field). For the pasture/dairy sites, nitrate-N concentrations decreased substantially in samples from MW7 and MW11 during the 4-year period (**Figure 4a**). In contrast, nitrate-N concentrations in samples from MW12 increased from 32 mg/L in January 2013 to 66 mg/L in December 2016, with a high concentration of 77 mg/L in September 2016. Another potential source was noted for the high nitrate-N concentrations in samples from MW12. There may have been a permitted yard debris disposal site near or upgradient from the field where MW12 is located (D. Bottcher, personal communication, SWET, Inc., 2015).

For wells near irrigated cropland, nitrate-N concentrations in MW2, MW4, and MW10 increased during the four-year period. Slight increases in nitrate-N concentrations were observed in samples from MW3 and MW13. Nitrate-N concentrations decreased in MW18 (**Figure 4b**) and remained relatively constant in MW1 and MW20 from 2013 to 2016.

For wells near nonirrigated pastures/hayfields, nitrate-N concentrations in MW14 decreased to 5.8 mg/L in September 2016 from a peak concentration of 16 mg/L in August 2014. Nitrate-N concentrations increased substantially in MW5, going from 2.9 mg/L in January 2013 to 9.0 mg/L in September 2016. Slight increases in nitrate-N concentrations were recorded in MW9 and MW16 (**Figure 4c)**, although levels in MW15 and MW16 remained consistently low (<0.5 mg/L) from 2013 to 2016.

For wells near residential areas, nitrate-N concentrations remained consistently low (<0.5 mg/L) in MW6 and MW8. Nitrate-N concentrations in MW17 increased slightly from 2013 to 2016 and remained nearly the same in AAK7015 (2.6 to 3.4 mg/L, near the Newberry domestic wastewater spray field) (**Figure 4d**).

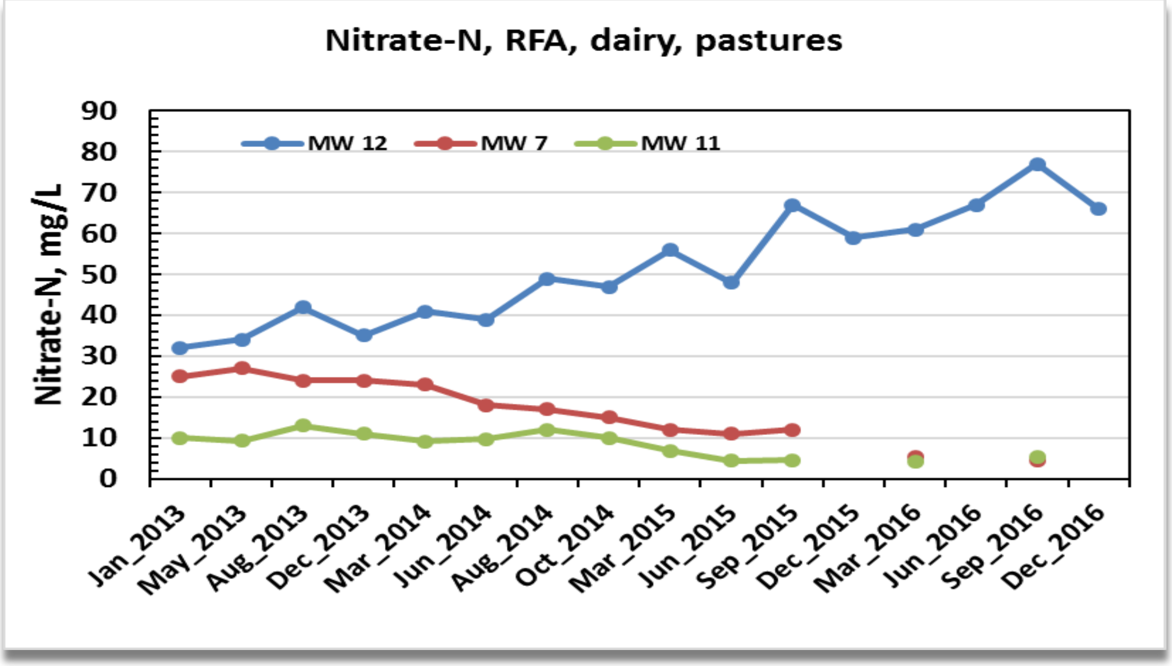

Figure 4a. Nitrate-N concentrations in RFA groundwater samples collected from wells near dairy and pasture land uses, 2013–16

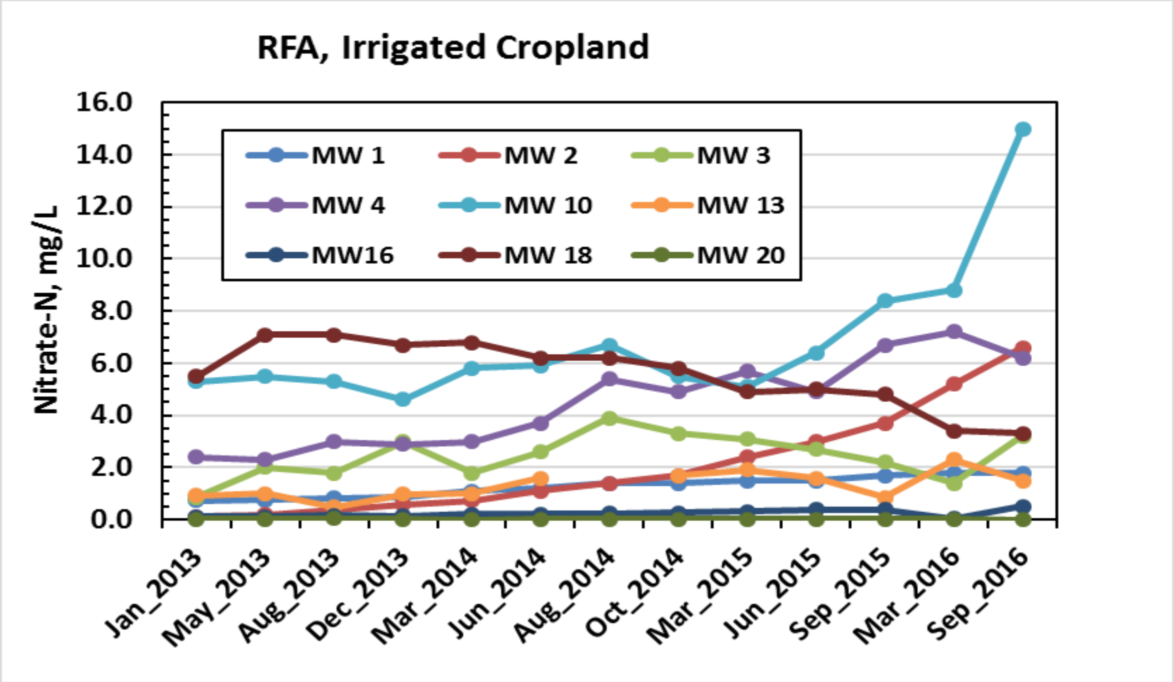

Figure 4b. Nitrate-N concentrations in RFA groundwater samples collected from wells near irrigated cropland land uses, 2013–16

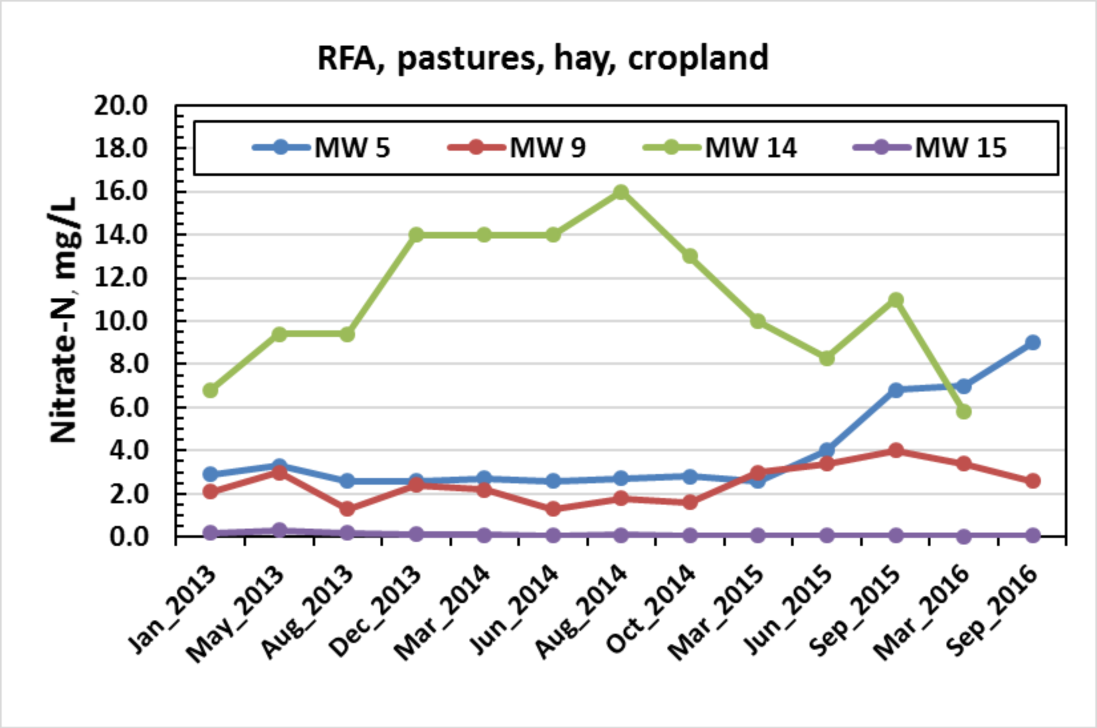

Figure 4c. **Nitrate-N concentrations in RFA groundwater samples collected from wells near nonirrigated pasture, hayfield, and cropland land uses, 2013–16**

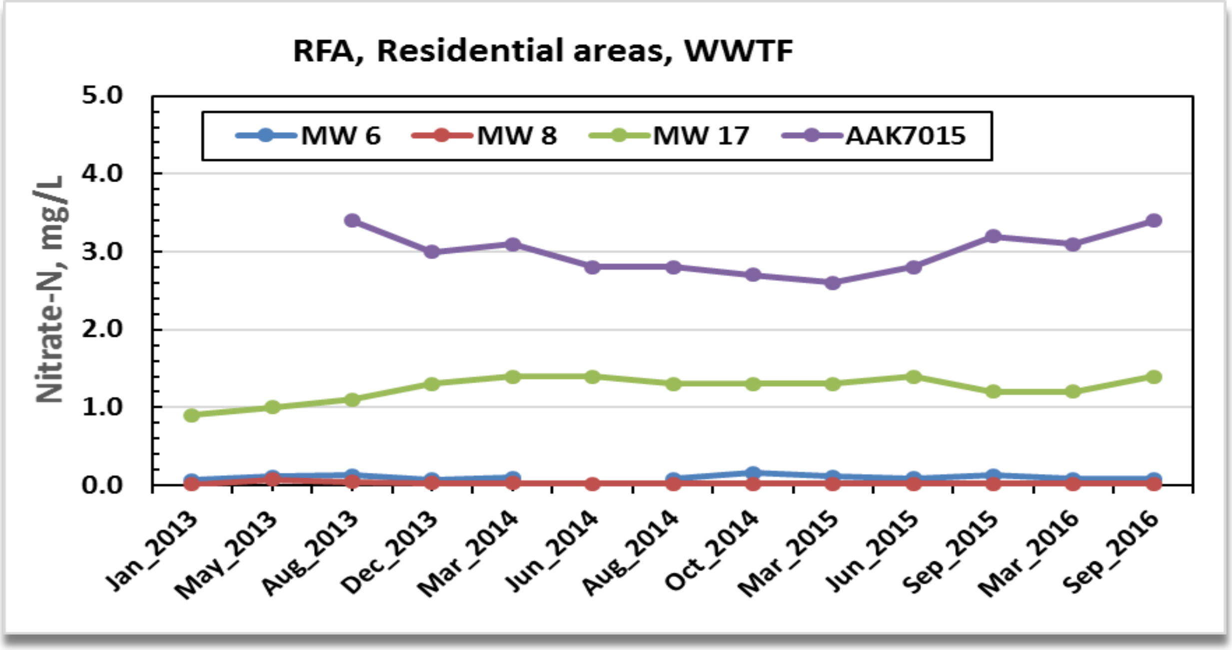

Figure 4d. **Nitrate-N concentrations in RFA groundwater samples from wells near residential and WWTF land uses, 2013–16**

Groundwater Levels and Nitrate-N Concentrations

Changes in groundwater levels reflect variations in rainfall and subsequent recharge to the aquifer. **Figure 5** shows monthly rainfall amounts during the study period at the SRWMD Forest Grove station near the RFA. **Figure 6a, Figure 6b, Figure 6c,** and **Figure 6d** illustrate the changes in groundwater levels from 2013 to 2016 for wells grouped by land use categories.

Statistical analyses were made to determine the relation between changes in groundwater levels and nitrate concentrations. There was a statistically significant ($p<0.05$) increase in nitrate-N in groundwater levels measured in 6 monitoring wells (MW7, MW13, MW14, MW16, MW17, and MW18) from 2013 to 2016. In samples from 2 wells (MW7 and MW18), there were statistically significant decreases in nitrate-N concentrations during the 4-year period. In MW15, groundwater levels increased, but at a slightly lower statistical significance level ($p<0.07$), and nitrate-N concentrations showed a significant decreasing trend at this site. In samples from 3 wells (MW13, MW14, and MW17), no trends in nitrate-N concentrations were found. Samples from the other wells did not show any trends (increasing or decreasing) over time.

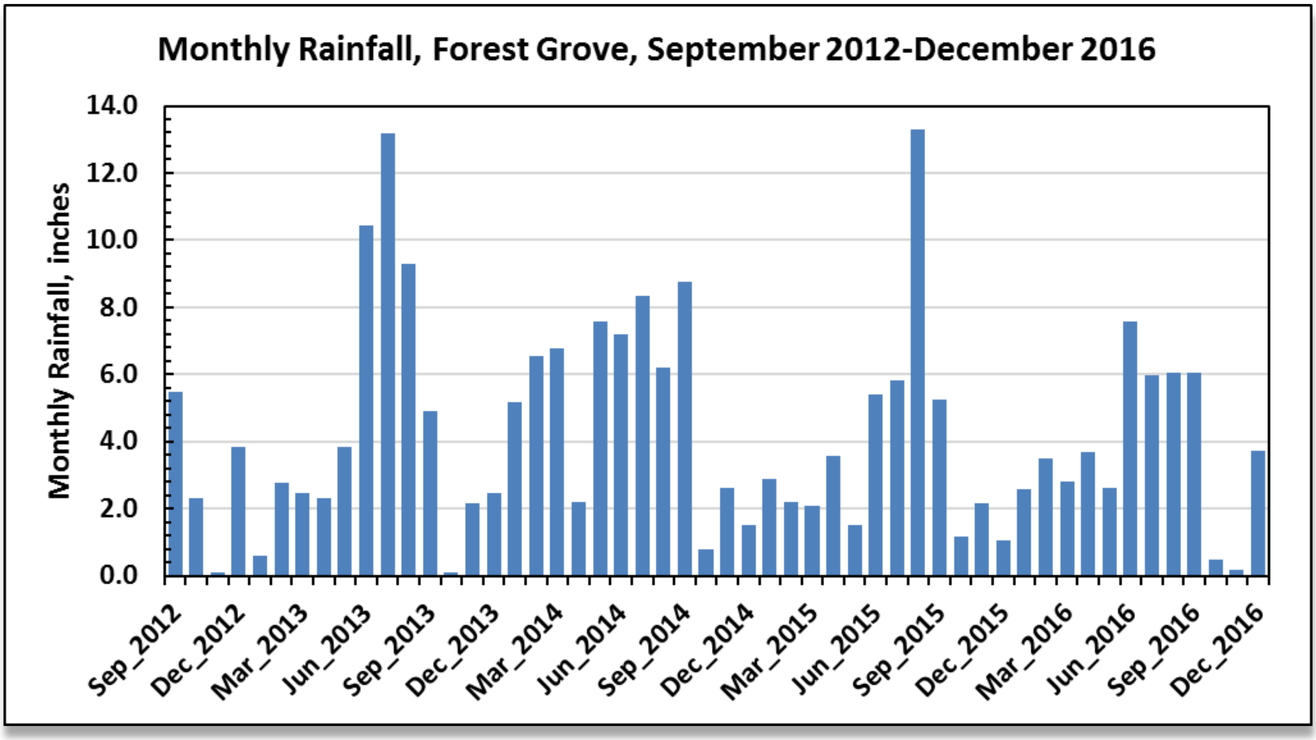

Figure 5. Monthly rainfall totals at the SRWMD Forest Grove station, near Newberry, Florida, September 2012–December 2016

The increase in groundwater levels and corresponding decrease in nitrate-N concentrations in MW7 (dairy, pasture), MW15 (nonirrigated pastures, hay, cropland), and MW18 (irrigated cropland) may partly be related to dilution but more likely to changes in agricultural practices (described in additional detail later). The significant increase in nitrate-N concentrations and the corresponding increase in groundwater levels at MW16 (irrigated cropland) are also likely related to changes in agricultural practices.

Groundwater levels only increased at well sites located in the southern two-thirds of the study area. Several factors may account for this increase, including soil drainage, depth to groundwater, and agricultural practices. Five wells (MW7, MW13, MW15, MW16, and MW18) are located near irrigated fields. During the four-year period, there were no statistically significant correlations between nitrate-N concentrations and groundwater levels in wells near irrigated or nonirrigated sites.

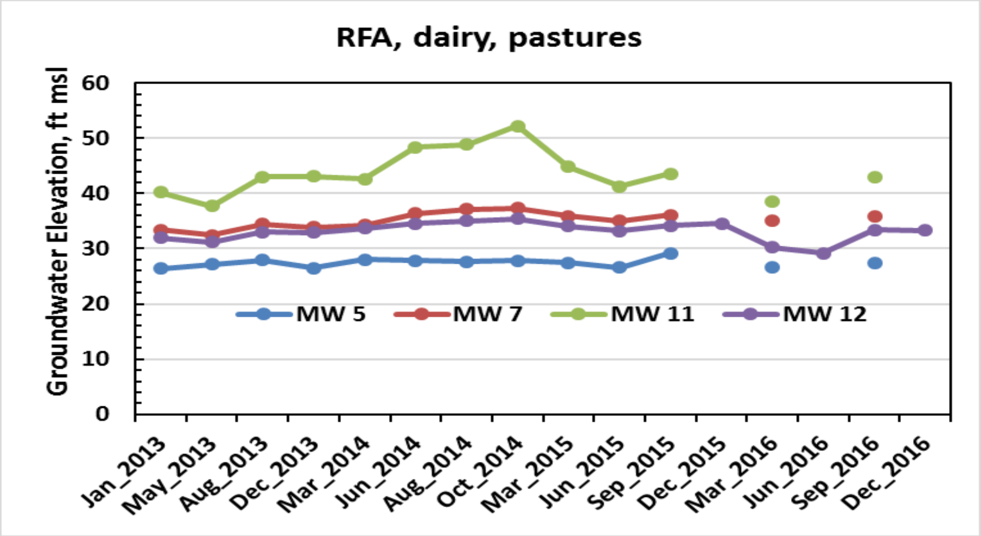

Figure 6a. Changes in groundwater levels at wells near dairy and pasture land uses, 2013–16

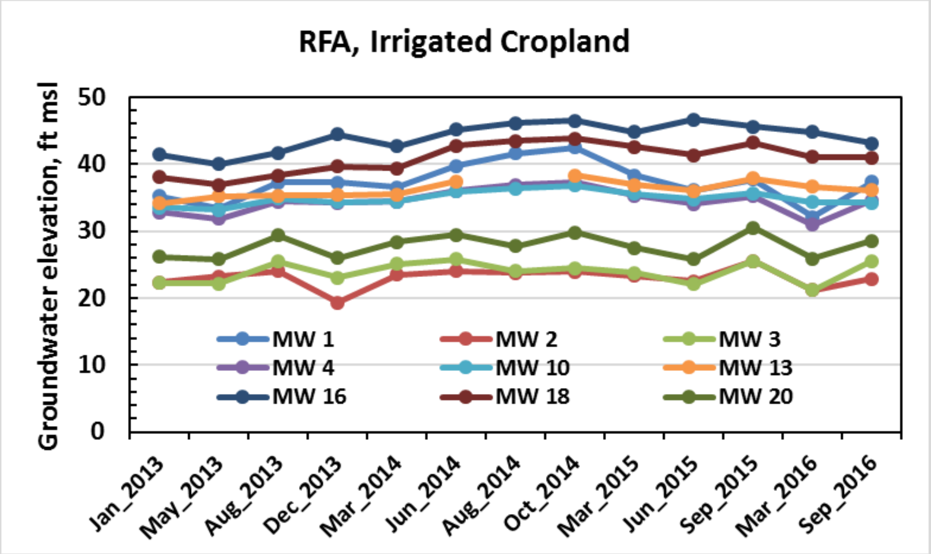

Figure 6b. Changes in groundwater levels at wells near irrigated cropland land uses, 2013–16

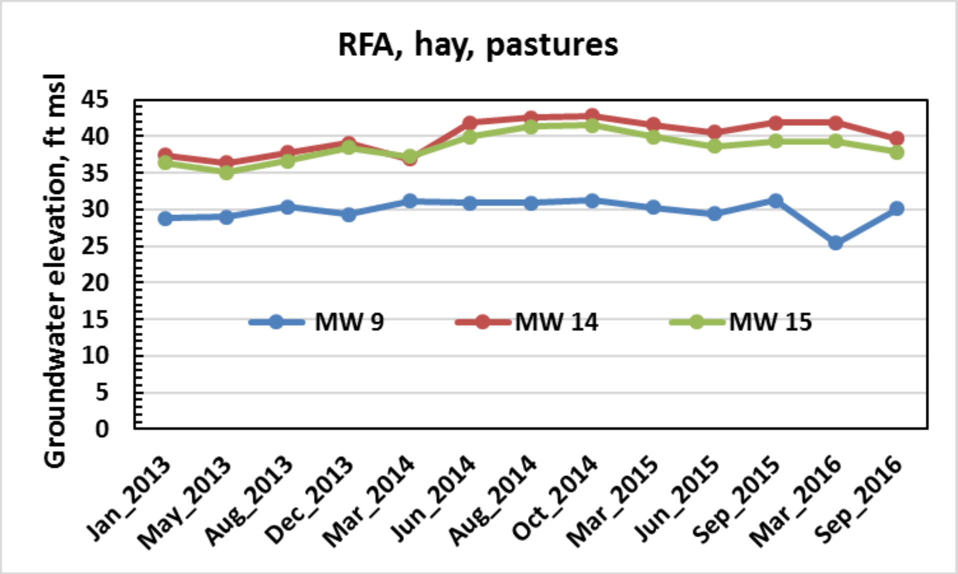

Figure 6c. Changes in groundwater levels at wells near hay and pasture land uses, 2013–16

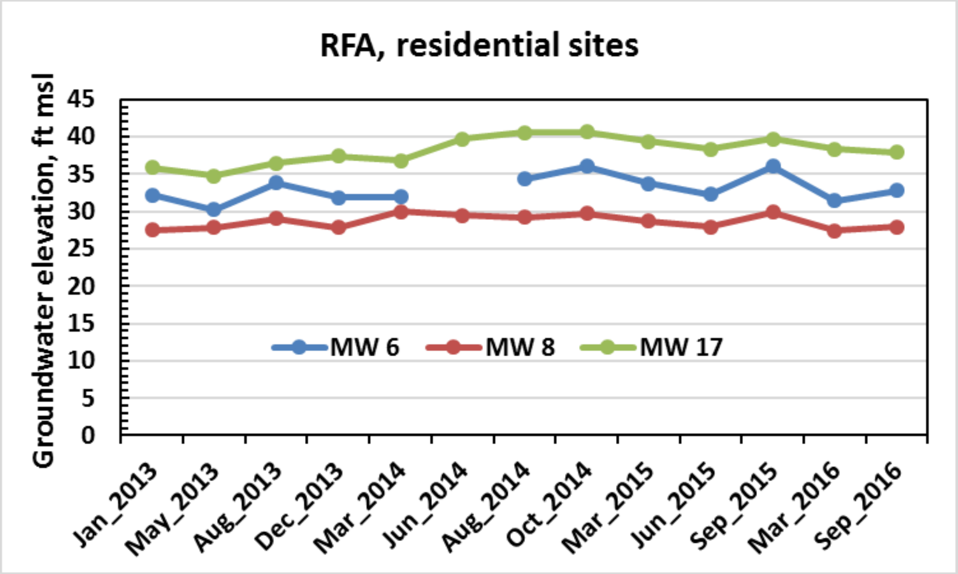

Figure 6d. Changes in groundwater levels at wells near residential land uses, 2013–16

Springs and River Water

From 2013 to 2016, nitrate-N concentrations in samples of spring water remained relatively constant and elevated above 1 mg/L (**Figure 7**). The following narrow ranges of nitrate-N concentrations were observed during this period for the 4 monitored springs in the RFA: Gilchrist Blue Spring (2.0 to 2.4 mg/L), Ginnie Spring (1.0 to 1.7 mg/L), Devil's Eye Spring (1.4 to 2.0 mg/L), and Twin Spring (0.9 to 1.3 mg/L). Nitrate-N concentrations in all 4 sampled springs continued to exceed 0.35 mg/L from 2013 to 2016. This concentration is the TMDL for springs in the Santa Fe River BMAP area.

From 2013 to 2016, nitrate-N concentrations in river water samples were consistently lower than in springs, but the former showed considerably more fluctuation from one quarterly sample to another than did the springs samples (**Figure 7**). The river samples were collected over a wide range of discharge conditions (846 to 2,690 cfs), as measured at the U.S. Geological Survey (USGS) Santa Fe River station near Fort White (**Figure 8**). There was a significant inverse relation between nitrate-N concentrations and discharge in samples collected at the Fort White site (Spearman's rho=-0.63, p=0.039) and at the State Road (SR) 47 Bridge site (Spearman's rho=-0.63, p=0.037) (**Figure 9**). The inverse relation between nitrate-N and discharge likely indicates that higher nitrate-N concentrations are originating from groundwater inflow to the river during low-flow conditions, and nitrate-N concentrations are being diluted with upstream waters with low nitrate-N concentrations during high-flow conditions.

Nitrate-N concentrations were consistently lower in samples from the river site upstream from Poe Spring. There appears to be an inverse relation between nitrate-N concentrations and discharge at the river site upstream from Poe Spring. However, there was no statistically significant trend (Spearman's rho= -0.46, p=0.16). These lower nitrate-N concentrations may reflect a greater amount of denitrification in groundwater because of nitrate-reducing conditions near the river in this area.

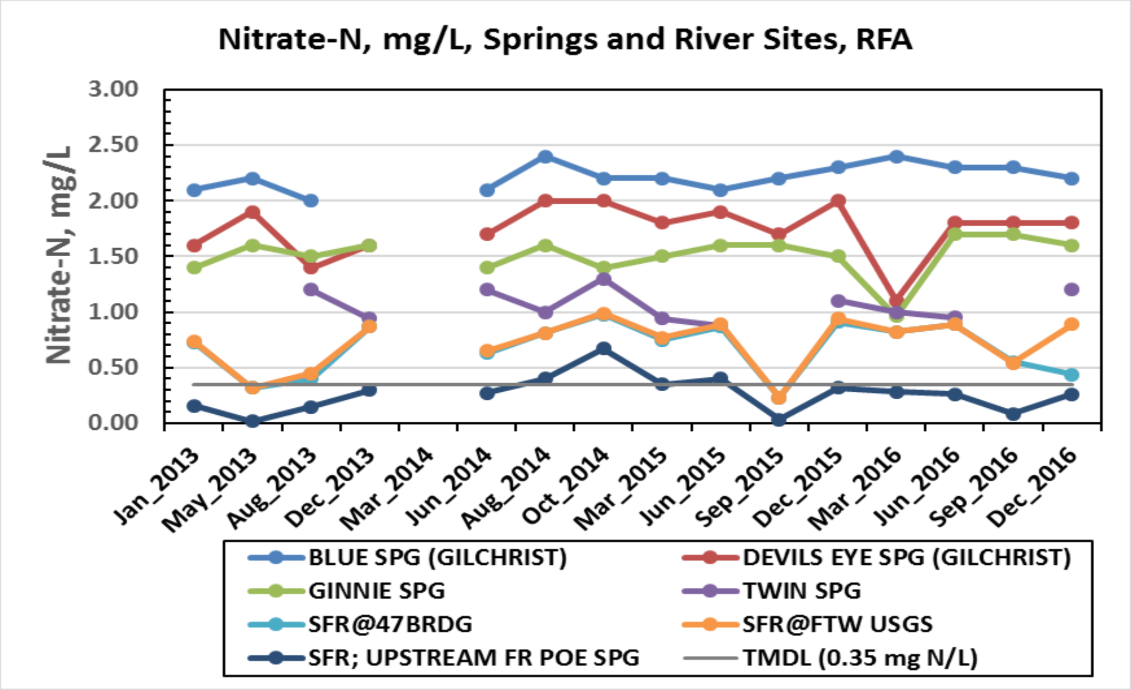

Figure 7. Nitrate-N concentrations in springs and river water samples, 2013–16. No samples were collected from springs or river sites in March 2014 or from Twin Spring in the extreme high-water conditions of September 2015.

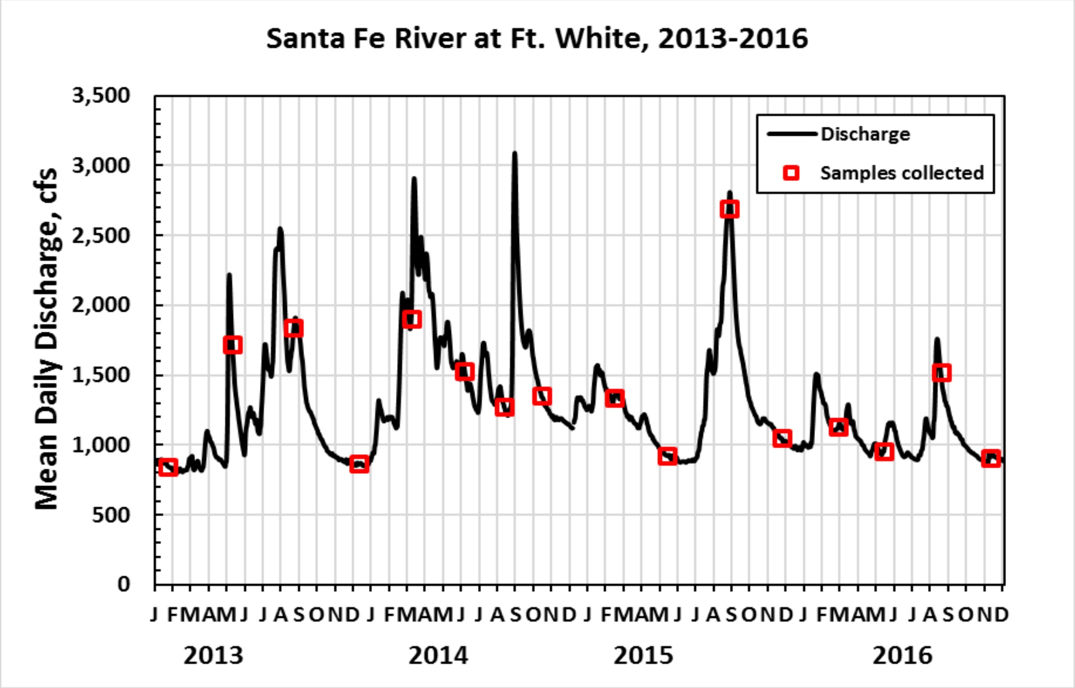

Figure 8. **Mean daily discharge for the Santa Fe River near Fort White, January 2013–December 2016 (USGS data), and collection dates for river water samples**

River water samples were collected during a variety of flow conditions (Figure **8**). There was a statistically significant inverse correlation between nitrate-N concentrations in river water samples and discharge at Fort White (**Figure 9**). The decrease in nitrate-N concentrations at higher flows likely results from the dilution of elevated nitrate concentrations in groundwater and springs by low nitrate-N concentrations in upstream river water.

Continuous Monitoring Data at Ginnie Spring

The continuous water quality data—along with information on rainfall, spring flow velocity, and Santa Fe River discharge—provide a more complete understanding of short-term interactions between river water and the groundwater discharging from Ginnie Spring, and how these interactions affect nitrate concentrations in the spring. This section summarizes the continuous water quality data measured using various sensors (SC, DO, pH, temperature, and nitrate-N). Figure 10 shows the continuous measurements for DO, nitrate-N, temperature, SC, and pH from January 1, 2015, through December 31, 2016.

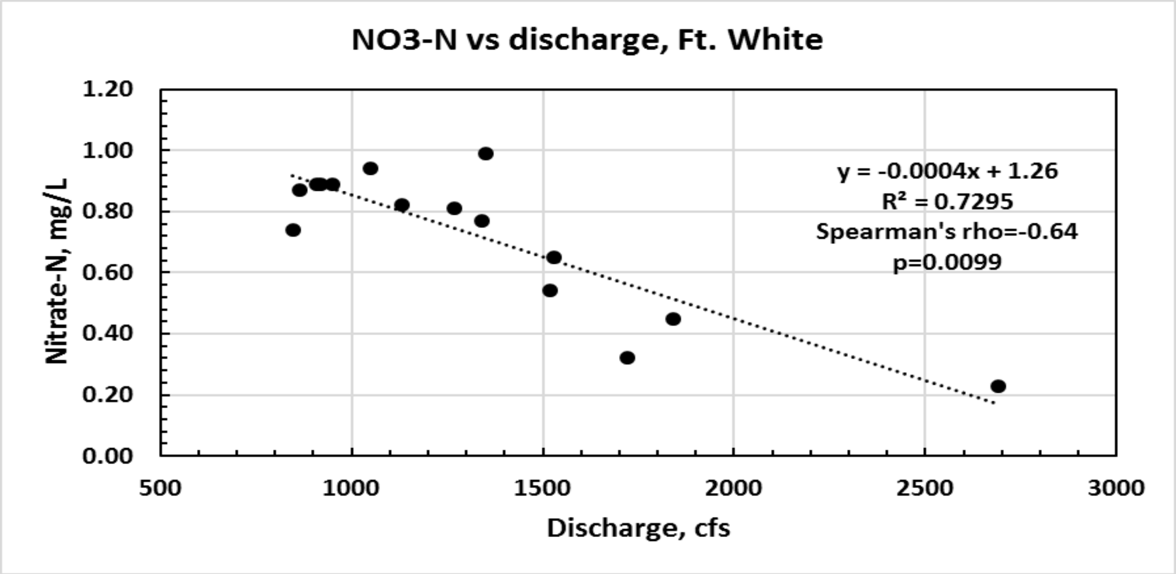

Figure 9. Relation between discharge and nitrate-N concentrations in water samples from the Santa Fe River near Fort White, January 2013–December 2016 (discharge data from USGS Caribbean-Florida Water Science Center)

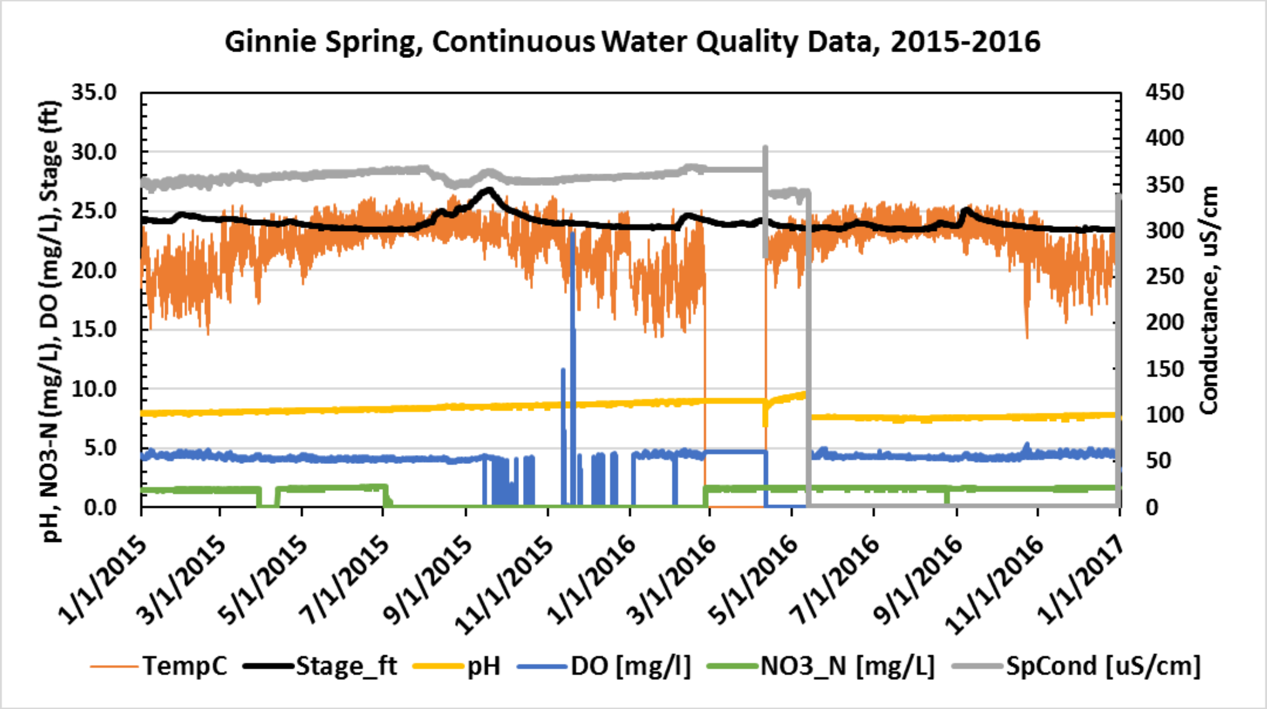

Figure 10. Continuous measurements of water quality (hourly averages), Ginnie Spring, 2015–16

Data for the various continuous monitoring sensors were missing from several periods from 2015 to 2016. Prior to 2015, SC and DO measurements stabilized in mid-July 2014 after an erratic start in June 2014 following sensor installation. The nitrate sensor (SUNA) was not operative for two weeks in April 2015 and from July 2015 through February 2016, when it went in for service (**Figure 10**). The DO sensor malfunctioned in September 2015, and no DO data were measured for the remainder of 2015 and for two weeks in late April and early May 2016.

During 2015 and 2016, problems persisted with the continuous temperature sensor measurements that could have affected other water quality parameters. Because the water is pumped from the spring to a flow-through cell for the sensor measurements, the water temperature of the spring water sample is affected by the air temperature in the shelter and in the flow-through cell. The fluctuations in spring water temperatures measured in the flow-through cell are affected by changes in air temperature in the shelter throughout the 24-hour period, for example, as shown for December 2015 (**Figure 11**).

These fluctuations in temperature also appear to be causing subtle changes in some water quality parameters that likely are not representative of conditions in groundwater discharging from the spring. An increase in water temperature can cause an increase in the mobility of ions in solution and the dissociation of molecules, and this would lead to an increase in SC. The fluctuations in nitrate-N concentrations that are similar to changes in SC throughout the day also appear to be related to changes in air temperature in the shelter and not actual changes in the aquifer.

Conversely, as water temperatures increase, the solubility of oxygen and other gases decreases, and DO values decrease. Consequently, pH also increases with higher temperatures, as less carbon dioxide (CO_2) gas is present. In December 2016, the DEP contractor installed a higher volume pump and increased the purge frequency to the sensor flow cells. This should help alleviate the temperature-related anomalies. An important quality control check on the accuracy of the readings from the continuous water quality sensors is to compare these data with field-calibrated measurements. Due to several SUNA malfunctions from 2015 to 2016, there were some missing nitrate-N concentrations for comparison with laboratory analyses of grab samples. However, during this period, most SUNA-measured nitrate-N concentrations closely matched (±0.1 mg/L) nitrate-N concentrations in field-collected spring water samples analyzed by the DEP Laboratory (**Table 2**).

The one exception was on March 22, 2016**,** when the SUNA-measured nitrate-N concentrations were 1.62 mg/L compared with the laboratory-measured concentration of 0.96 mg/L. A similar decrease in nitrate-N concentration was observed in Devil's Eye Spring for the March 2016 sample, and the lower nitrate-N concentration in both Ginnie and Devil's Eye Springs may be related to the influx of river water from the high discharge in the Santa Fe River from mid- to late February 2016 (**Figure 8**). An increase in Ginnie Spring stage and a decrease in velocity are consistent with an influx of river water (**Figure 12**).

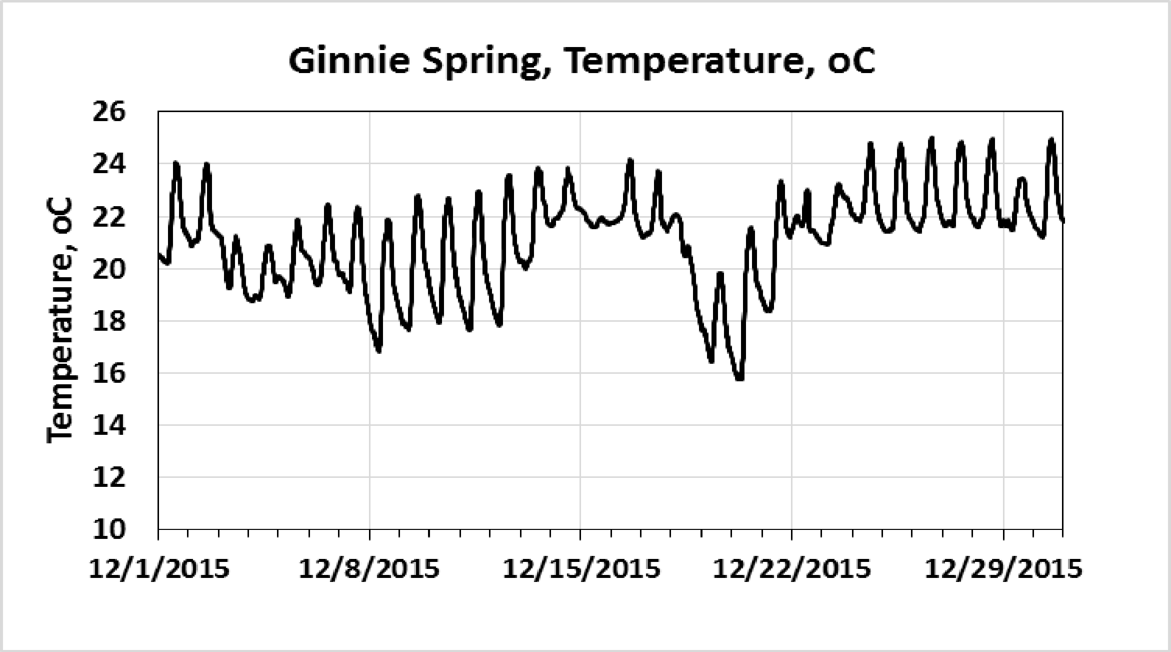

Figure 11. Continuous measurements of water temperature from Ginnie Spring, December 2015 (expanded view)

Continuous sensor conductivity measurements were slightly higher (5 %–6 %) than those measured in the field during sample collection from March 2015 to March 2016. For the June, September, and December 2016 samples, the continuous conductivity measurements and the field conductivity measurements agreed within 2 %.

Continuous pH sensor measurements were consistently 0.3 units or higher than field measurements from 2015 to 2016, indicating that the pH sensor likely is not providing accurate pH measurements. The continuous DO measurements are 0.3 to 0.5 mg/L lower than the field measurements (except for the December 2016 sample), and likely are affected by the changes in temperature when water is pumped from the spring to the flow-through chamber and the incomplete purging of water from previous samples from the chamber. Depending on when the water sample was collected and the outside air temperature, the continuous temperature sensor measurements were either lower or higher than field temperature measurements (**Table 2**).

There was a weak correlation between continuous measurements of daily rainfall amounts at Ginnie Spring and those measured at the SRWMD Forest Grove station (**Figure 13**). This likely is related to local variations in rainfall (particularly for thunderstorms) but may also be related to malfunctions of the rainfall gauge at Ginnie Spring.

Table 2. Comparison of data from continuous monitoring equipment at Ginnie Spring with field and laboratory measurements

NM = Not measured because of sensor malfunction.
µs/cm = Microsiemens per centimeter; su = Standard units

	Date	Time	Conductivity uS/cm	pH su	DO mg/L	Temp °C.	NO_3_N	mg/L
Field YSI	3/2/15	1645	338	7.51	4.56	22.85	Lab	1.5
Continuous	3/2/15	1645	359	8.04	4.14	23.80	Continuous	1.45
Field YSI	6/2/15	1621	337	7.50	4.30	23.0	Lab	1.6
Continuous	6/2/15	1615	362	8.22	3.99	23.57	Continuous	1.66
Field YSI	9/15/15	1520	339	7.30	4.60	22.80	Lab	1.6
Continuous	9/15/15	1515	360	8.51	4.08	26.65	Continuous	NM
Field YSI	12/15/15	1413	340	7.40	4.00	22.20	Lab	1.5
Continuous	12/15/15	1415	358	8.72	NM	23.70	Continuous	NM
Field YSI	3/22/16	1411	349	7.20	4.60	22.5	Lab	0.96
Continuous	3/22/16	1410	366	8.99	4.64	NM	Continuous	1.62
Field YSI	6/8/16	1445	353	7.10	4.90	23.3	Lab	1.7
Continuous	6/8/16	1445	346	7.61	4.14	24.9	Continuous	1.62
Field YSI	9/14/16	1440	352	7.00	4.3	23.7	Lab	1.7
Continuous	9/14/16	1445	345	7.58	4.11	24.37	Continuous	1.58
Field YSI	12/6/16	1624	347	7.4	1.64	22.4	Lab	1.6
Continuous	12/6/16	1630	342	7.7	4.43	21.39	Continuous	1.62

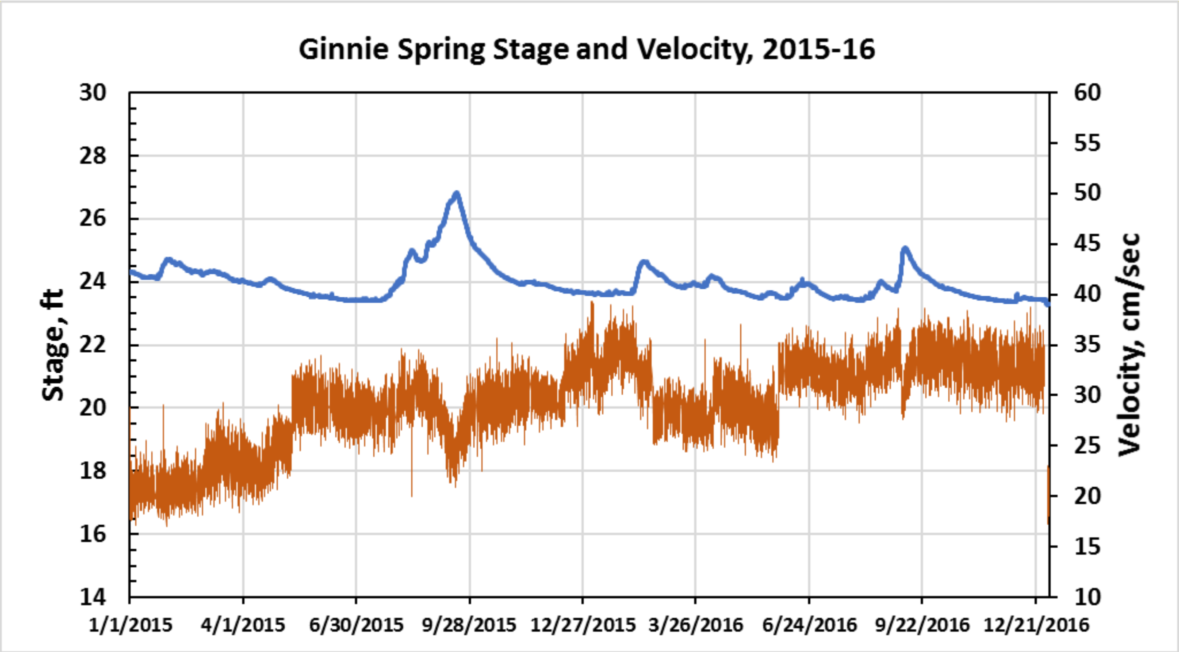

Figure 12. Continuous measurements of flow velocity (centimeters per second [cm/s]) and stage (feet) at Ginnie Spring, January 2015–December 2016

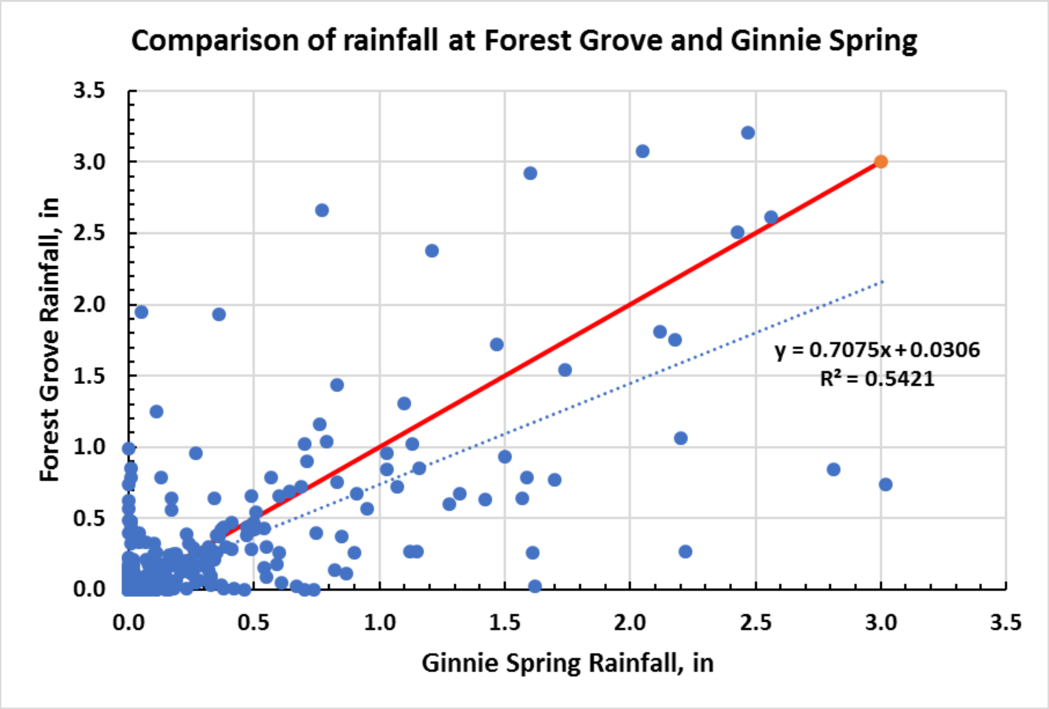

Figure 13. Comparison of daily rainfall amounts at Forest Grove and Ginnie Spring, 2015–16

Nitrate Isotopes

The stable isotope signatures of nitrate, including delta N-15 of nitrogen, $\delta^{15}N\text{-}NO_3$, and delta O-18 of oxygen, $\delta^{18}O\text{-}NO_3$, have been used effectively to attribute nitrate in groundwater and surface waters to specific sources. There typically is some overlap between the ranges of isotopic values for different sources, However, values of $\delta^{15}N\text{-}NO_3$ less than 5 parts per thousand (ppt) generally indicate an inorganic N source (synthetic fertilizer), while values of $\delta^{15}N\text{-}NO_3$ greater than 8 ppt generally indicate an organic N source (animal or human wastes). Also, the 2 isotopes of nitrate are useful in assessing denitrification, which generally leads to a 2:1 increase in the ratio for $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values.

Water samples from most wells (14 of 20) had average N isotope values less than or equal to 5 ppt, which is consistent with an inorganic fertilizer source of N (**Figure 14**). Groundwater samples from MW5, MW7, MW11, MW12, MW15, MW16, and MW20 had $\delta^{15}N\text{-}NO_3$values that fluctuated between 5 and 9.5 ppt, which likely indicates a mixed inorganic and organic source of N (**Figure 14**).

The values of $\delta^{15}N\text{-}NO_3$ in groundwater samples (January 2013–June 2015) fluctuated from 2 to 3 ppt but remained below 5 ppt in 10 of the RFA monitoring wells (**Figure 15**). The $\delta^{15}N\text{-}NO_3$ values in water samples from MW11 decreased from 9.6 ppt in January 2013 to 6.3 ppt in June 2015, while the nitrate-N concentration remained close to 10 mg/L from January 2013 to

October 2014, but decreased to 4.4 mg/L in June 2015. This well is located 40 feet from an irrigated crop field and pasture that support a dairy, which has been in operation since before 1994. The top of the well screen is 38 feet below the land surface.

Changes in agricultural practices likely account for the shift from a mixed nitrogen source to an inorganic nitrogen source. Denitrification is not likely occurring, as the $\delta^{15}N\text{-}NO_3$ values have decreased and DO levels in the aquifer are generally greater than 4 mg/L. Water samples from Well AAK7015, next to the Newberry spray field where treated wastewater is applied to a grassed area, had an isotopic composition consistent with a domestic wastewater source. There does not appear to be any consistent trend in $\delta^{15}N\text{-}NO_3$ values with time or with nitrate concentrations in any of the monitoring wells. However, $\delta^{15}N\text{-}NO_3$ values for the June 2015 samples from most wells tended to be lower than previous values.

Samples of spring water have a nitrate isotopic composition consistent with an inorganic nitrogen source (**Figure 14**). Santa Fe River water samples downstream from Ginnie Spring had a nitrate isotopic signature consistent with a mixed source of nitrogen, while the nitrate isotopic composition of Santa Fe River water samples upstream from Poe Spring indicated that denitrification likely has occurred (**Figure 12**).

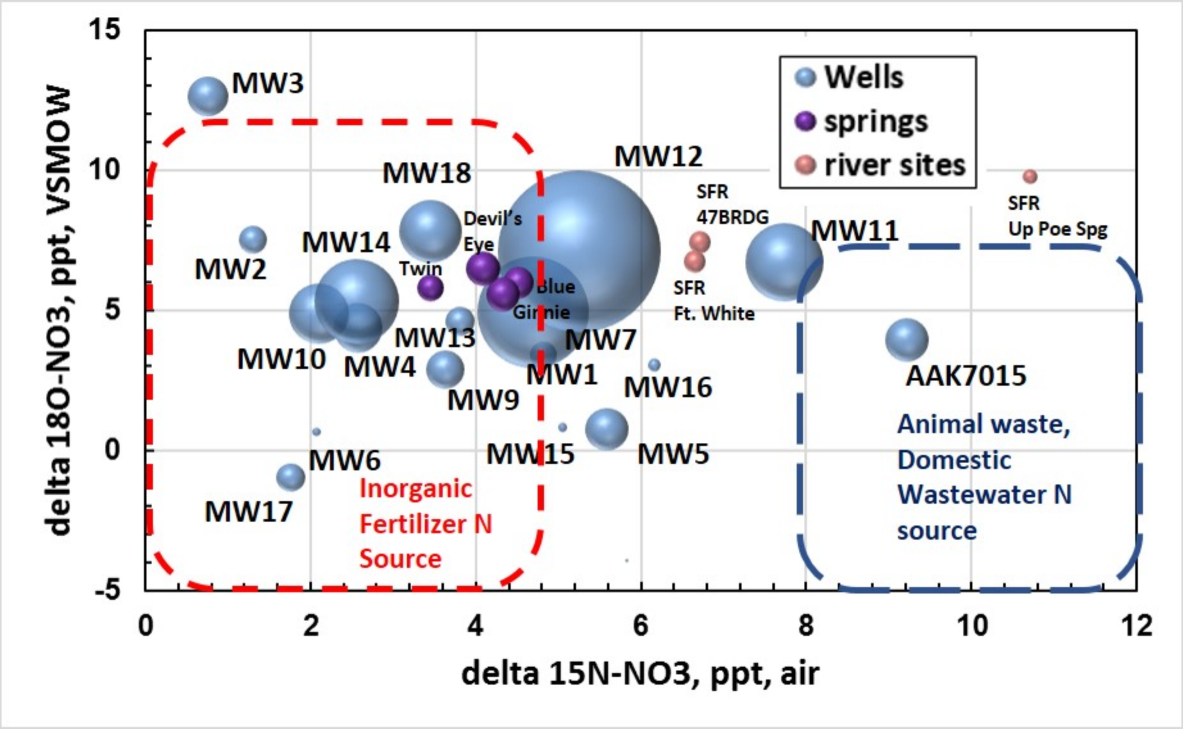

Figure 14. **Average nitrate isotopic composition in water samples from wells, springs, and river sites, January 2013–June 2015. Symbol size is proportional to average nitrate-N concentration.**

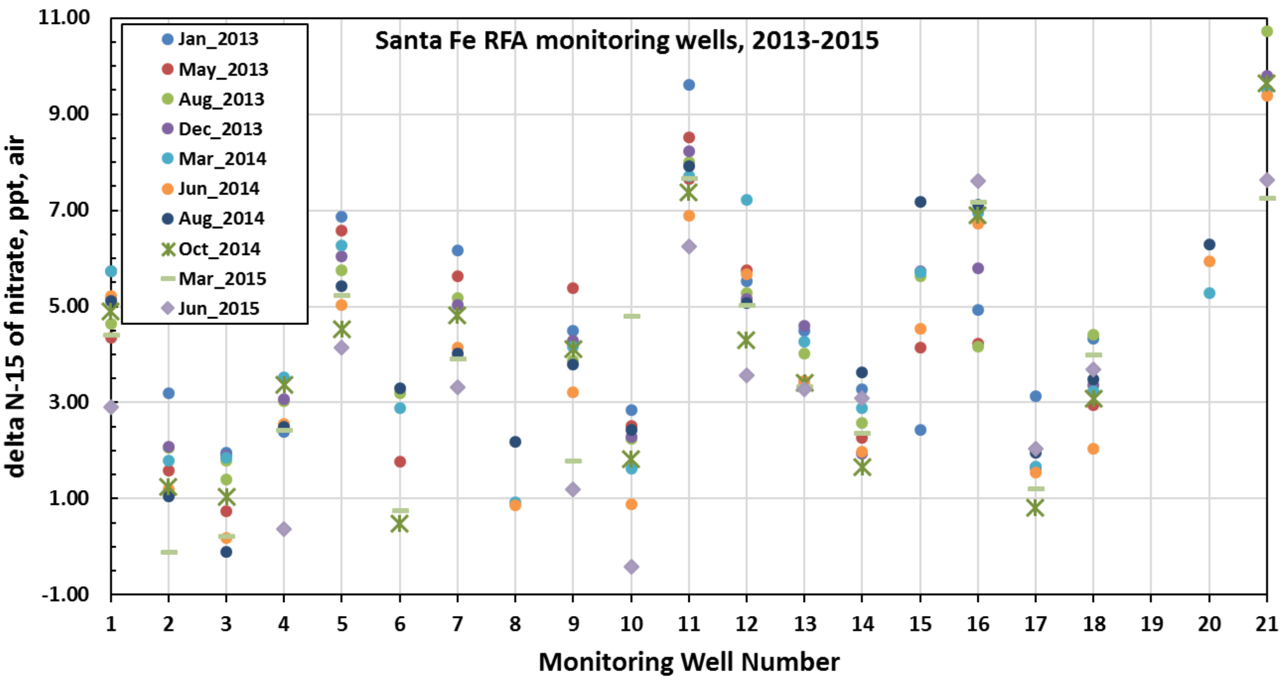

Figure 15. Plot showing the variations in δ^{15}N of nitrate in water samples collected from monitoring wells, January 2013–June 2015

Other Water Quality Data

Potassium

Potassium is a major component of synthetic fertilizers, along with nitrogen and phosphorus. Although not a constituent of concern under the BMAP, potassium can be a useful indicator of a fertilizer source. However, the relationship between nitrate-N and potassium is not as straightforward as one might expect, given that the nitrate isotope data indicate that fertilizers are the dominant source of nitrate-N in the RFA. It is important to note that fertilizer composition and application rates can change over time depending on the needs of the crop type.

Sites with the highest nitrate-N concentrations tend to be associated with low potassium values, and sites with the highest potassium concentrations tend to have low nitrate-N concentrations (**Figure 16**). For example, water from MW12 had the highest nitrate-N concentration, but potassium concentrations were less than 1.5 mg/L. Potassium concentrations in MW7 (pasture supporting dairy) steadily increased from 1.2 mg/L in January 2013 to 10.9 mg/L in September 2016. The potassium concentrations in MW14, located near a hayfield, increased from 0.98 mg/L in January 2013 to 2.20 mg/L in March 2016. Nitrate-N concentrations in MW14 also remained elevated but decreased from a peak concentration of 16 mg/L in August 2014 to 5.8 mg/L in March 2016.

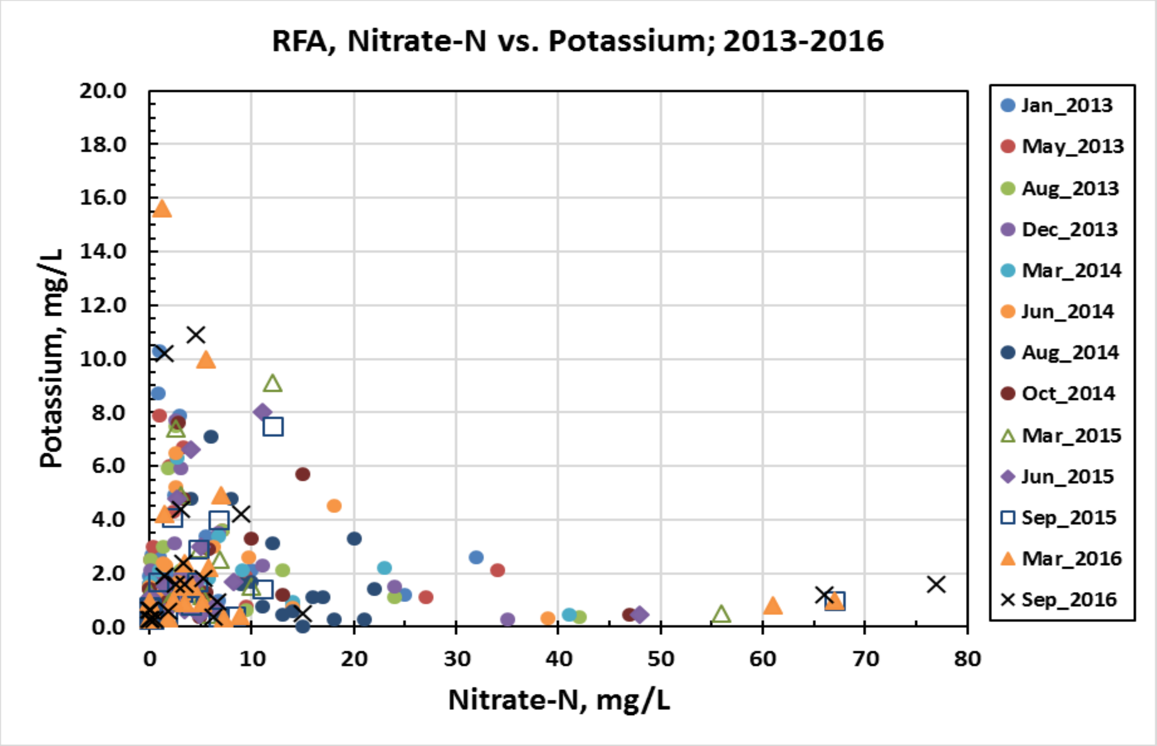

Figure 16. Relation between nitrate-N and potassium in water samples from RFA monitoring wells, 2013–16

Potassium concentrations remained elevated in wells near dairies and associated pastureland (**Figure 17a**). There was a large increase in potassium concentrations in MW7 from 1 to 11 mg/L from 2013 to 2016. However, nitrate-N concentrations showed a large decrease during this period.

For wells near irrigated cropland areas, potassium concentrations remained relatively constant in samples collected throughout the 3-year period. However, potassium concentrations decreased in MW3 and MW4 (**Figure 17b**). There was a statistically significant correlation (Spearman's rho=0.45, $p<0.0001$) between potassium and nitrate-N in wells near irrigated cropland.

For wells near nonirrigated pastures and hayfields, potassium concentrations generally remained below 2 mg/L, except for MW5 and MW9. MW5 had elevated potassium concentrations (> 6 mg/L) until June 2015, followed by a decrease to 4.2 mg/L in September 2016 (**Figure 17c**). There was an inverse correlation (Spearman's rho=-0.30; p=0.01) between potassium and nitrate-N concentrations in wells near nonirrigated cropland and hayfields.

In wells near residential areas, potassium concentrations remained above 10 mg/L in MW17 but decreased substantially from the peak concentration of 120 mg/L in August 2013 (**Figure 17d**). The high concentrations at this location are surprising, given that MW17 is situated in Newberry, where land use is classified as urban. However, the elevated concentrations may result from past agricultural practices. Another possible source of potassium in groundwater at this site (MW17) is a fertilizer plant that operated from 1965 to sometime in the 1980s (S. Tucker, OAWP, 2017, written communication). The plant, located a quarter-mile east-southeast of MW17, burned down in the 1980s. Potassium concentrations in the 3 other wells near residential areas remained low and unchanged.

The potassium concentration in groundwater is also affected by the thickness and type of clays and other materials that overlie the Upper Floridan aquifer (UFA) at each site. Potassium and other positively charged ions (cations, calcium [Ca], magnesium [Mg], and sodium [Na]) are adsorbed by negatively charged sites on clay minerals and soils. Water samples from wells with the highest potassium concentrations (particularly MW17, but also MW3, MW5, MW7, MW9, and MW18) tend to occur at sites where the depth to limestone is generally less than 20 feet below the land surface. Conversely, lower potassium concentrations were found in water samples from wells at sites where the thickness of sands and clays overlying the UFA was greater.

Potassium concentrations in spring waters fluctuated between 0.3 and 0.70 mg/L during the 4-year period (**Figure 18**), considerably lower than potassium concentrations in most well samples. Higher potassium concentrations were found in Blue and Devil's Eye Springs (Gilchrist County) compared with Ginnie and Twin Springs. Potassium concentrations in the 2 Gilchrist County springs also showed a steady increase from December 2015 to December 2016.

Potassium concentrations in river water samples tended to fluctuate more than in spring samples (**Figure 19**). Similar concentrations were measured in samples from the Santa Fe River at SR 47 Bridge and at the USGS station at Fort White (generally 0.60 to 1.0 mg/L). Higher concentrations were found in water samples from the Santa Fe River upstream from Poe Spring. These correspond to the higher potassium concentrations in Gilchrist Blue Spring and Devil's Eye Spring compared with Ginnie and Twin Spring.

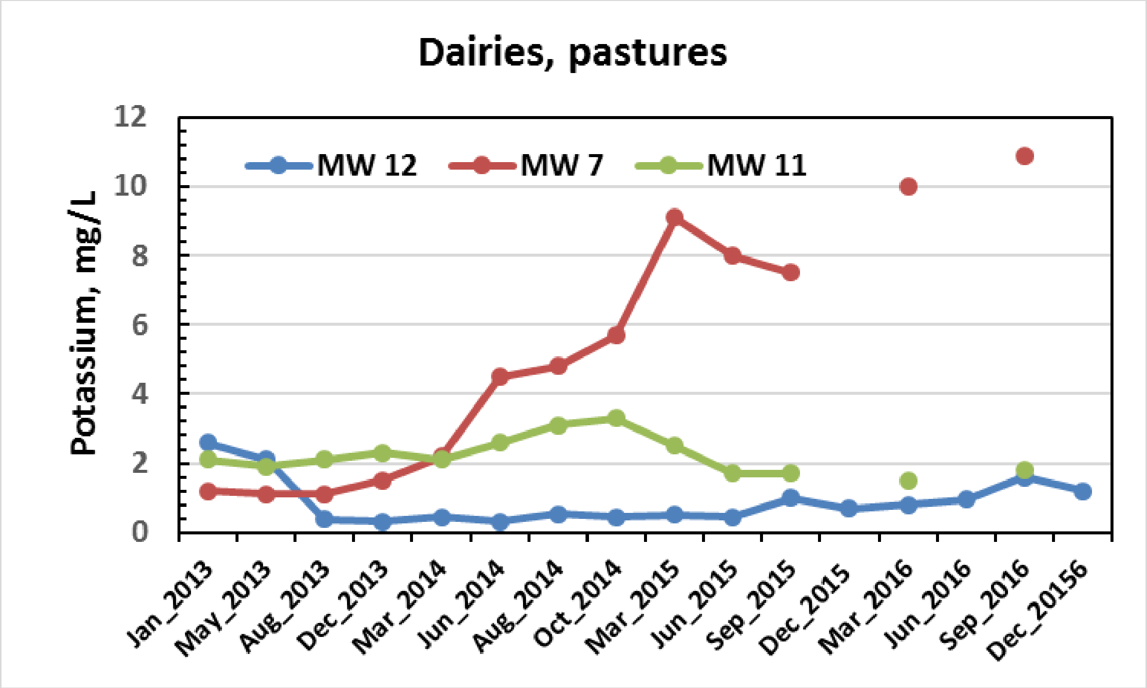

Figure 17a. Potassium concentrations in water samples from wells near dairies and pastures in the RFA, 2013–16

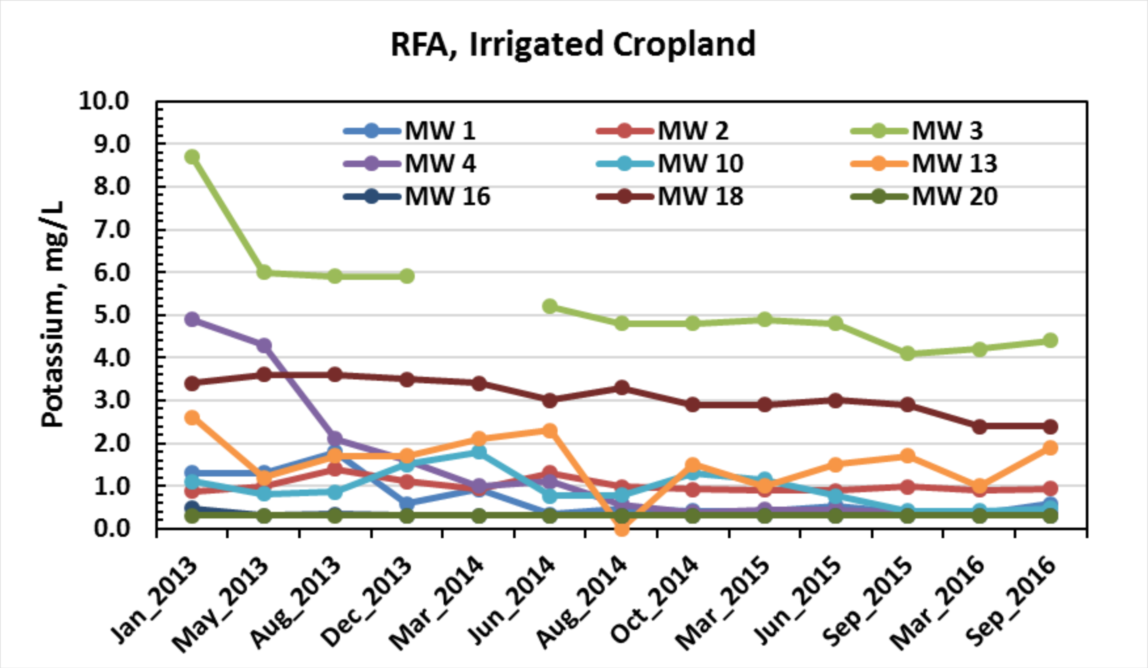

Figure 17b. Potassium concentrations in water samples from wells near irrigated cropland in the RFA, 2013–16

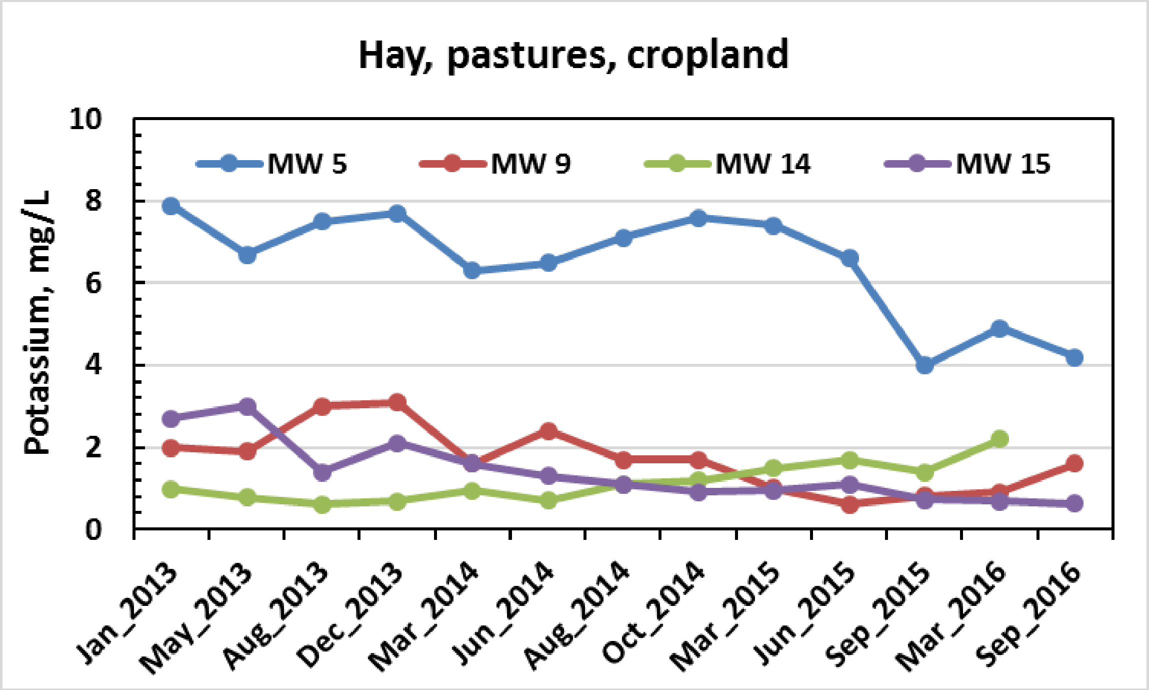

Figure 17c. **Potassium concentrations in water samples from wells near hayfields, pastures, and cropland in the RFA, 2013–16**

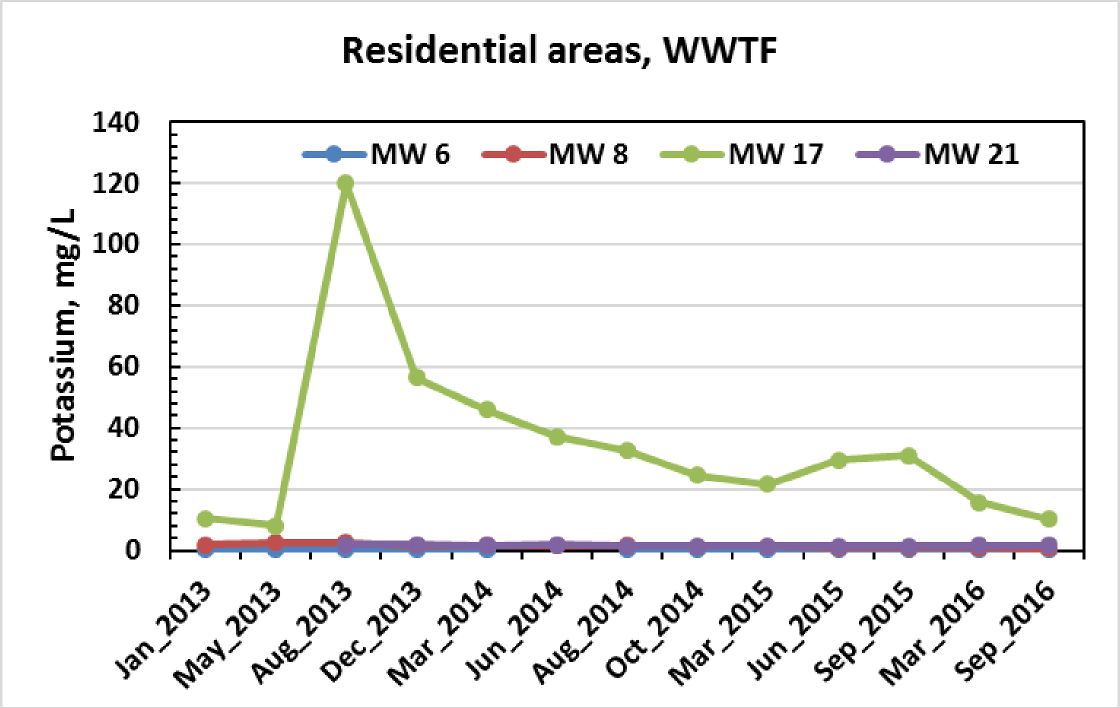

Figure 17d. **Potassium concentrations in water samples from wells near residential areas and a WWTF in the RFA, 2013–16**

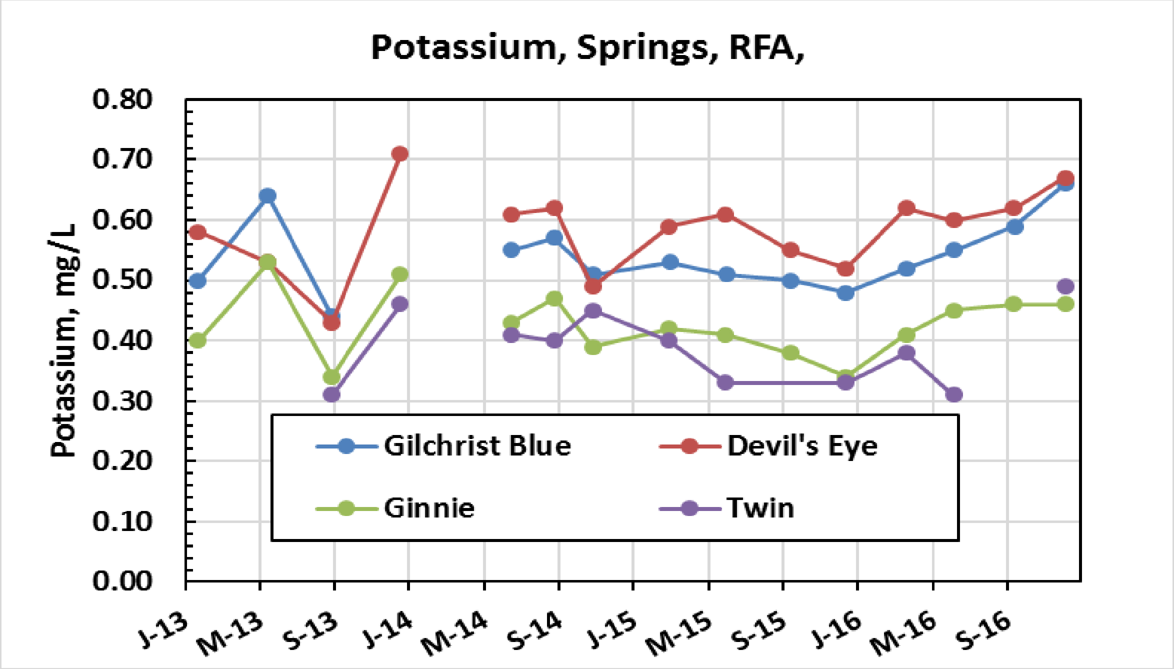

Figure 18. Potassium concentrations in RFA spring water samples, 2013–16

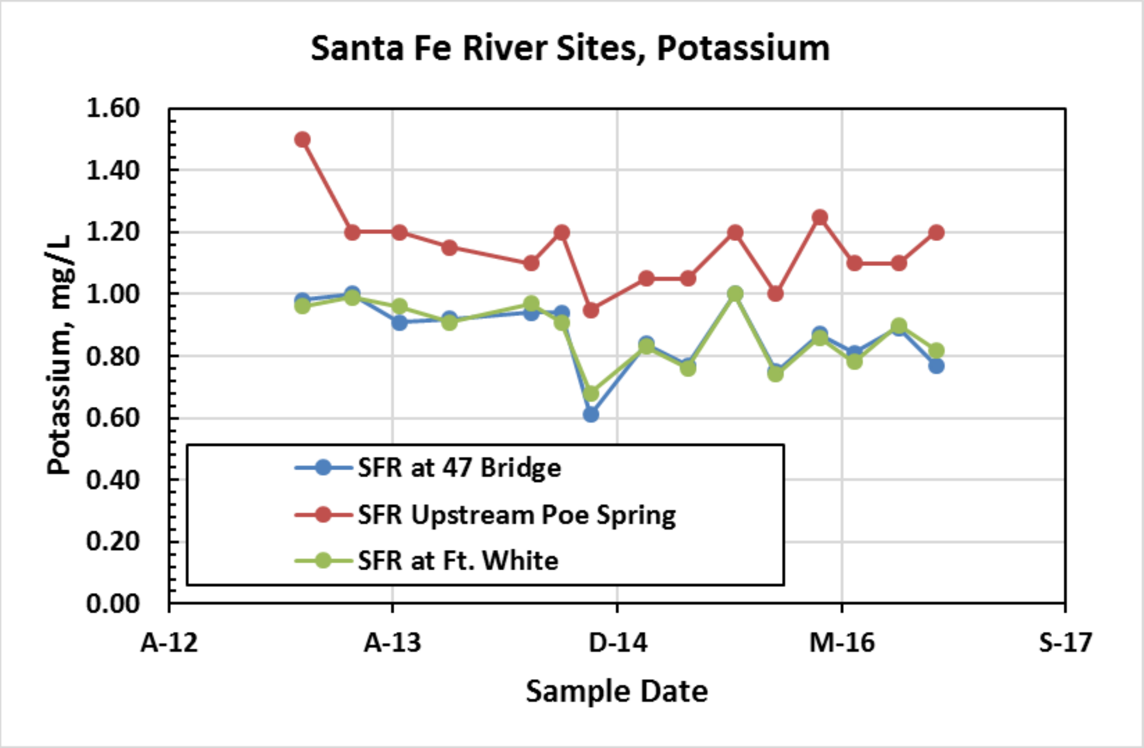

Figure 19. Potassium concentrations in RFA river water samples, 2013–16

Sulfate

Sulfate concentrations in most monitoring wells ranged from 1 to 10 mg/L. There was a statistically significant correlation between nitrate-N and sulfate concentrations in wells near irrigated sites (p=0.0002). However, there was no correlation between nitrate-N and sulfate concentrations at wells near nonirrigated sites. MW17 and MW18 consistently had sulfate concentrations greater than 10 mg/L, although sulfate concentrations in MW17 decreased from a high concentration of 81 mg/L in August 2013 to 6.5 mg/L in September 2016. Likewise, potassium concentrations in MW17 also decreased substantially from the highest concentration of 120 mg/L in samples collected in August 2013 to 10.2 mg/L in September 2016.

A prior application of fertilizer containing potassium sulfate (K_2SO_4) could have accounted for the spike in potassium and sulfate concentrations in samples from MW17. The nitrate-N concentration only increased slightly from 1.0 mg/L (May 2013) to 1.4 mg/L (September 2016). However, nitrate isotope values were consistent with an inorganic nitrogen fertilizer source in samples collected during May and August 2013. Additional information on past land use practices near MW17 would likely help to explain the anomalously high potassium and sulfate concentrations in groundwater at this site. Another possible source of sulfate in groundwater at MW17 is a fertilizer plant, located a quarter-mile east-southeast of MW17, that operated from 1965 to sometime in the 1980s (S. Tucker, OAWP, 2017, written communication).

Water samples from MW18 continued to have high sulfate and calcium concentrations (250 and 195 mg/L in September 2015, respectively) and dissolved solids concentrations (643 and 661 mg/L in June and September 2015, respectively) compared with other groundwater samples, except for water from MW12. The elevated (excess) sulfate and calcium concentrations in water from MW18 (compared with other wells in the RFA) are consistent with the 1:1 molar ratio of calcium to sulfate found in gypsum ($CaSO_4$), which may have been applied as a soil conditioner (**Figure 20**).

Sulfate concentrations in spring waters from January 2013 to December 2016 ranged from 9.6 to 14 mg/L (median, 12 mg/L), and were slightly higher compared with most groundwater samples (except for the high concentrations found in samples from MW17 and MW18) (**Figure 21**). Two samples were collected from Poe Spring in January and May 2013, and sulfate concentrations ranged from 27 to 35 mg/L.

Sulfate concentrations in river water samples were considerably higher than in spring samples, ranging from 4.5 to 76 mg/L (**Figure 21**). During high-flow conditions, concentrations typically were less than 12 mg/L in samples from the 3 sites. At the Santa Fe River site upstream from Poe Spring, concentrations were considerably higher (4.5 to 76 mg/L) and showed more fluctuation than the 2 downstream river sites.

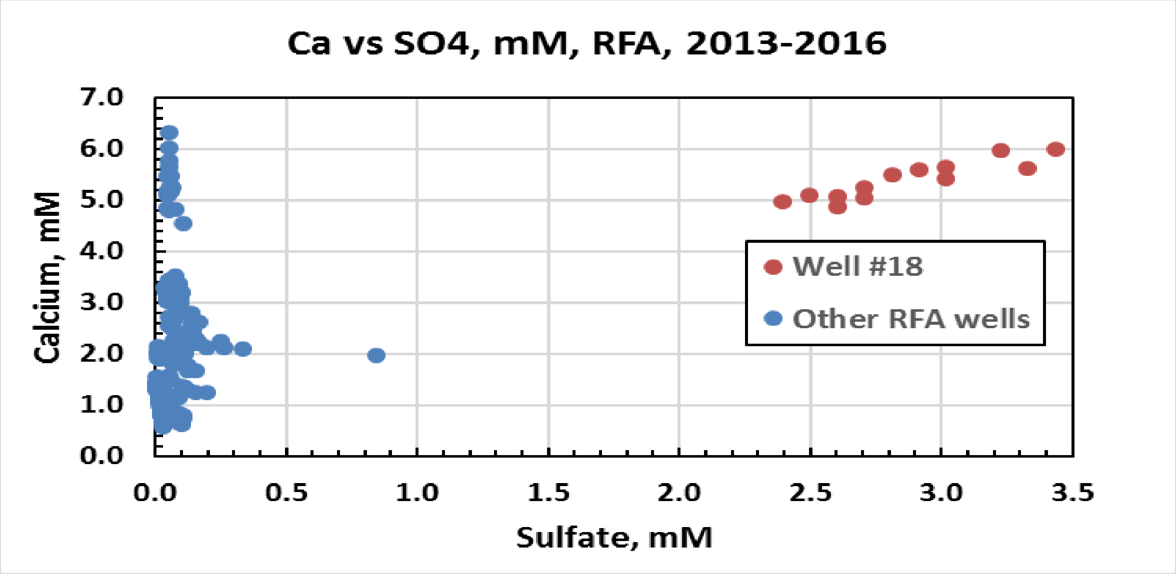

Figure 20. Excess sulfate (SO_4) and calcium (Ca) in RFA MW18, 2013–16, possibly resulting from the application of gypsum ($CaSO_4$) at the land surface as a soil conditioner

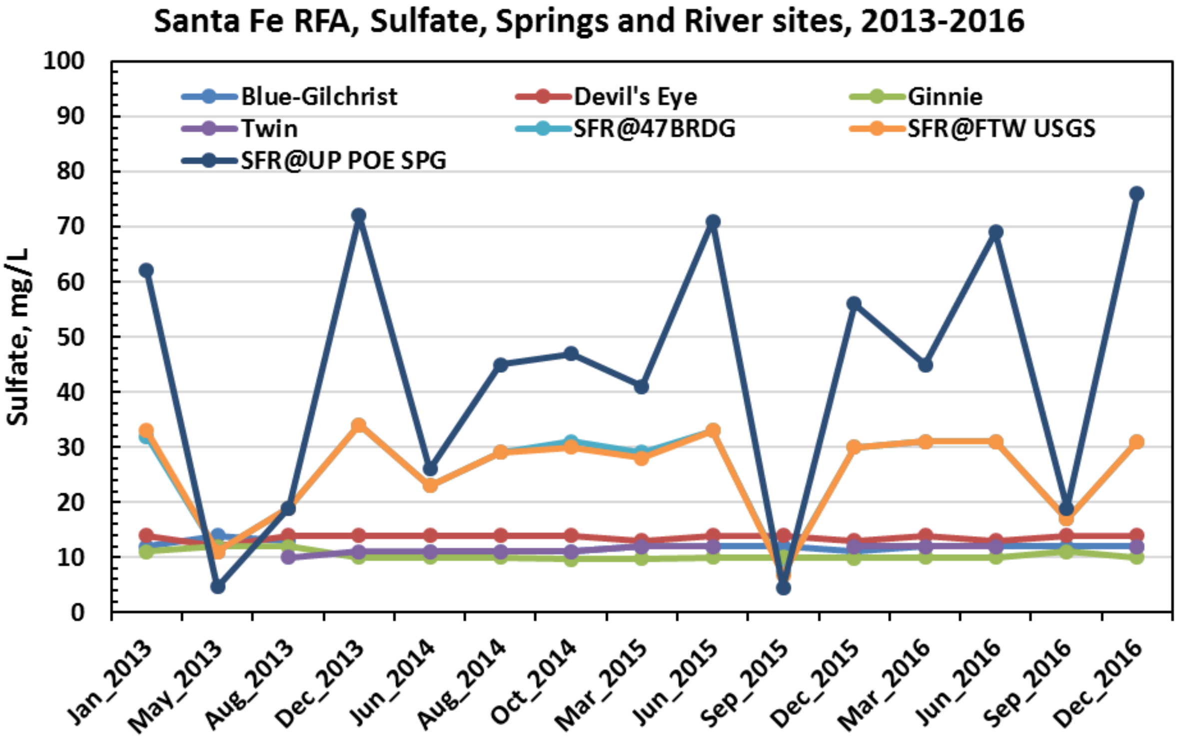

Figure 21. Sulfate concentrations in springs and river sites, 2013–15

Cl/Br Mass Ratio

The mass ratio of chloride to bromide (Cl/Br) also has been used to assess sources of solutes in groundwater and surface water (Panno et al. 2006; Alcalá and Custodio 2008). Relatively distinct ranges of the Cl/Br ratio have been reported for sewage and septic tank effluent, road salt, animal waste, atmospheric deposition, seawater, and landfill leachate (Katz et al. 2011). Although there was a considerable range in the Cl/Br mass ratio in water samples from each well, springs, or river site (**Figure 22** and **Figure 23**), sites with an inorganic nitrogen source (based on nitrate isotope data) generally have Cl/Br ratios below 400.

The range in Cl/Br mass ratios mainly results from dividing the relatively uniform chloride concentrations by fluctuations in the low bromide concentrations (usually less than 0.1 mg/L). The spike in the Cl/Br ratio for Ginnie Spring and Gilchrist Blue Spring in September 2015 was caused by the exceptionally low bromide concentrations in those samples (**Figure 23**).

Sites influenced by an organic nitrogen source or mixed source tend to have Cl/Br ratios greater than 500. MW12, MW15, and MW16 showed considerable variability of Cl/Br ratios from one sample to another and tended to plot in both the inorganic and organic nitrogen source areas. This may indicate that both sources are contributing nitrate to groundwater in these areas. The wells are located near residential developments containing septic tanks, which may explain the mixed N source. There is a statistically significant correlation between the Cl/Br mass ratio and $\delta^{15}N\text{-}NO_3$ concentrations in water samples from monitoring wells (Spearman's rho=0.53; $p<0.0001$). Therefore, the Cl/Br mass ratio may be useful as a surrogate for nitrogen isotopes as a nitrate-N source indicator (**Figure 24**).

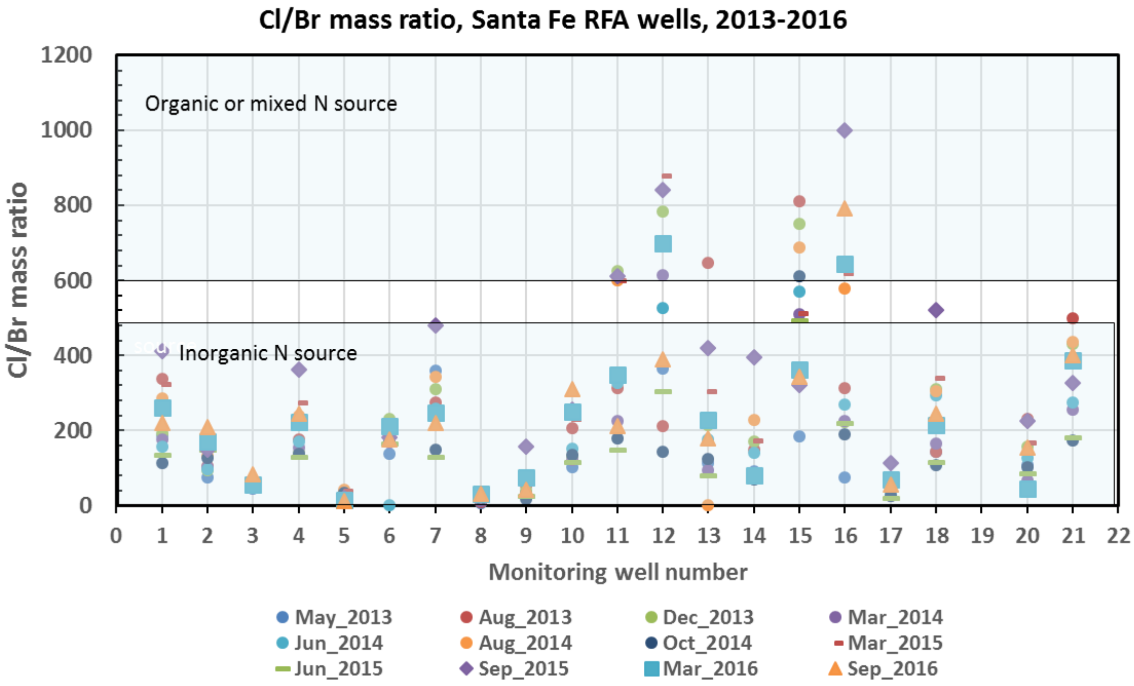

Figure 22. Variations in the Cl/Br mass ratio for water samples from monitoring wells, 2013–16

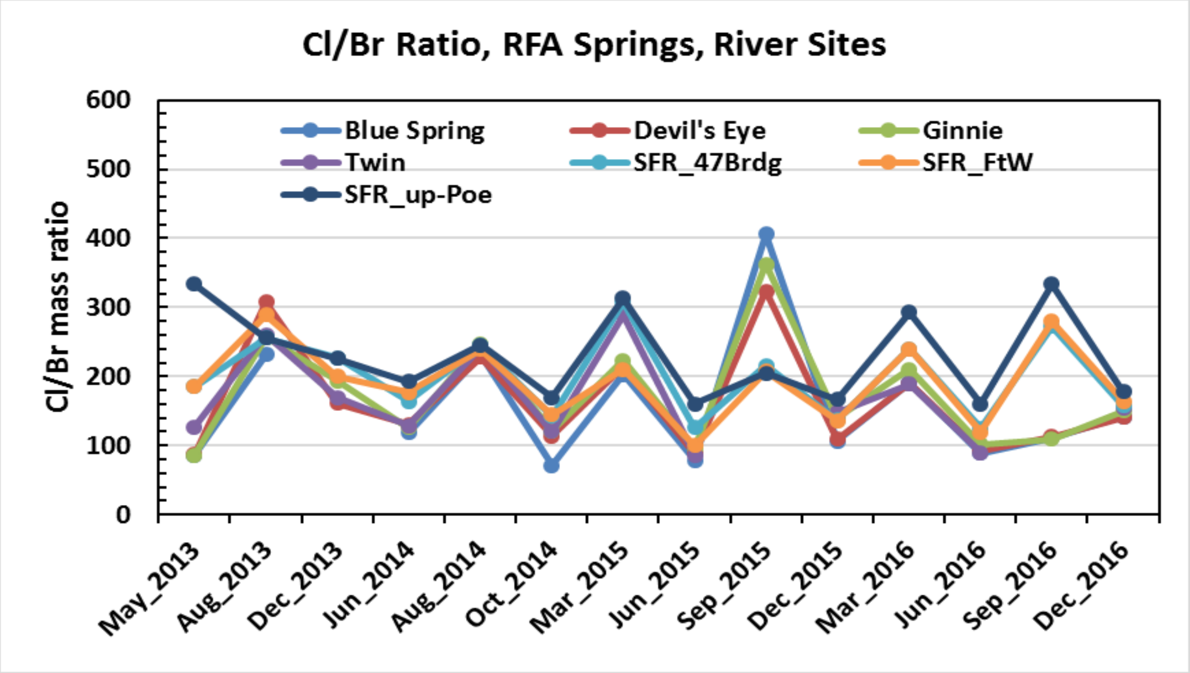

Figure 23. Variations in the Cl/Br mass ratio for water samples from springs and river sites, 2013–16

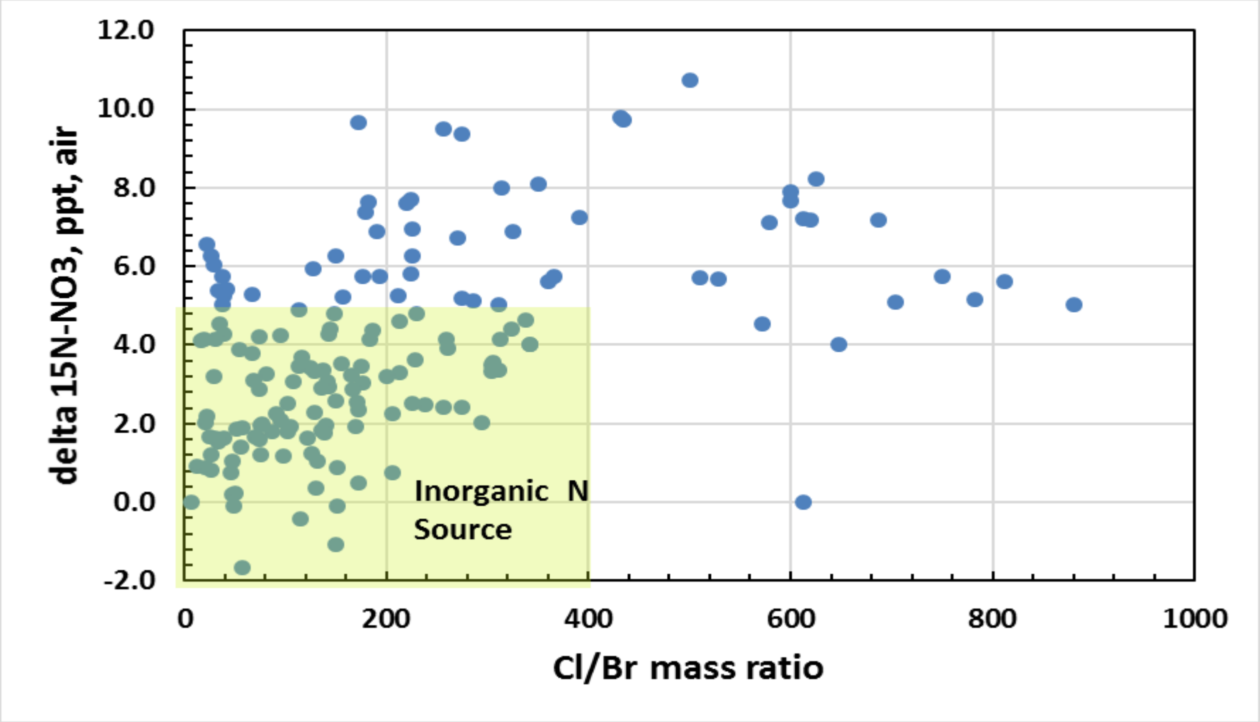

Figure 24. Plot showing the relation between the Cl/Br mass ratio and the $\delta^{15}N$ of nitrate for water samples from RFA monitoring wells, 2013–16

Pesticide Compounds

DEP collected water samples from monitoring wells in August 2014, October 2014, and June 2015 and analyzed them for the presence of numerous pesticide compounds (see **Appendix 4** for a complete list). Samples for pesticide analyses were collected from springs and river sites in August 2014, October 2014, and June 2015. Additional samples for pesticides were collected from Ginnie and Gilchrist Blue Spring in November 2014, and from Devil's Eye Spring in September and December 2015. Devil's Eye Spring was sampled as part of another DEP spring sampling water quality network. **Table 3** lists data for samples collected in August and October 2014 and June 2015, and **Table 4** lists data for samples collected in September and December 2015.

Herbicides were the only pesticide compounds detected (reported) in water samples from wells, springs, and river sites. Chlorpyrophos ethyl (an insecticide) was detected in water samples from Ginnie Spring, Twin Spring, and the Santa Fe River site upstream from Poe Spring. Atrazine, desethyl atrazine (an atrazine degradate), and hexazinone were the most frequently detected herbicides. Atrazine is a selective triazine herbicide used to control weeds in various crops and in conifer reforestation plantings. It does not adsorb strongly to soil particles and has a half-life of 60 to greater than 100 days. Hexazinone, also a triazine herbicide used to control weeds, is mostly used on noncrop areas. It has a half-life of less than 30 to 180 days.

Almost all reported values of herbicide compounds and chlorpyrophos ethyl were qualified by the DEP Laboratory as being between the laboratory method detection limit and the laboratory practical quantitation limit, or less than the criterion of detection (**Table 3**). Reported herbicide concentrations (nanograms per liter [ng/L]) in spring water samples were extremely low; a nanogram is one-thousandth of a microgram (µg).

Reported atrazine concentrations were higher in river water samples than in springs samples in June 2015 and August 2014. DEP did not collect any springs water samples for pesticide analyses in October 2014 (**Table 3**). Reported desethyl atrazine concentrations were higher than atrazine concentrations in water samples from Blue Spring and Ginnie Spring, but desethyl atrazine was not detected in Twin Spring in June 2015. Reported atrazine and desethyl atrazine concentrations were lower in river water samples collected in June 2015 than in samples collected in August and October 2014.

The higher reported concentrations of desethyl atrazine compared with atrazine in the August 2014 spring samples may indicate that the spring is discharging a small (nonquantifiable) component of groundwater that was recharged and moved through the system in anywhere from three months to possibly as much as a year. Atrazine was detected in the June 2015 samples from MW5, MW12, MW13, and AAK7015 but was not detected in any monitoring wells in the October 2014 samples. Desethyl atrazine was detected in samples from MW5, MW12, and MW13 in June 2015. Concentrations in MW13 were slightly lower in the samples collected in June 2015 than in October 2014.

Hexazinone also was reported in samples collected in June 2015 from MW20 and AAK7015, but not in MW4, where it was detected in October 2014. In June 2015, hexazinone was only detected in a sample from Gilchrist Blue Spring compared with detections in samples from Gilchrist Blue, Ginnie, and Twin Springs in August 2014. Bentazon was the only other reported herbicide in June 2015 samples from MW4, which had a detection in an October 2014 sample. No detections for 24-D were reported in June 2015 samples compared with the October 2014 samples from MW5 and MW6. Norflurazon was detected in samples from MW8, MW9, and MW18 in October 2014 but not in any samples collected in June 2015 (**Table 3**). Norflurazon is a pyridazinone herbicide used to control grass and broadleaf weeds. Its half-life in soils is 90 days. Norflurazon was not detected in any springs or river samples.

Samples collected from Devil's Eye Spring in September and December 2015 show a similar pattern of pesticide detections. All compounds listed in **Table 4** were detected at very low concentrations (ng/L) and all were qualified by the DEP Laboratory as being (1) at the laboratory method detection limit, (2) between the laboratory method detection limit and the laboratory practical quantitation limit, (3) an estimated value, or (4) less than the criterion of detection.

Table 3. Water samples from wells, springs, and river sites with detected concentrations of pesticides, August 2014, October 2014, and June 2015

ND = Not detected; Q = Qualifier code; NA = Not analyzed

		DEP SOP: LC-001-2(USGS O-2060-01)		EPA 8270D(method)									
FIELD ID	**DATE**	***analyte* (ug/L)**	**Q**	**ATRAZINE (ng/L)**	**Q**	**HEXAZINONE (ng/L)**	**Q**	**ATRAZINE DESETHYL (ng/L)**	**Q**	**NORFLURAZON (ng/L)**	**Q**	**CHLORPYRIFOS ETHYL(ng/L)**	**Q**
MW-4	10/29/2014	0.0021(Bentazon)	I	ND	U	0.42	T	0.29	I	ND	U	NA	
MW-5	10/27/2014	0.0058(2,4-D)	IQ	ND	U	ND	U	ND	U	ND	U	NA	
MW-6	10/27/2014	0.0048(2,4-D)	IQ	ND	U	ND	U	ND	U	ND	U	NA	
MW-8	10/21/2014	ND	U	ND	U	ND	U	ND	U	0.50	TQ	NA	
MW-8_dup	10/21/2014	ND	U	ND	U	ND	U	ND	U	0.62	TQ	NA	
MW-9	10/29/2014	ND	U	ND	U	ND	U	ND	U	0.90	T	NA	
MW-13	10/28/2014	NA		ND	U	ND	U	0.67	IQ	ND	U	NA	
MW-18	10/22/2014	ND	U	ND	U	ND	U	0.79	IQ	0.53	TQ	NA	
AAK7015	10/22/2014	ND	U	ND	U	45.00	QJ	0.20	TQ	ND	U	NA	
MW-20	10/21/2014	ND	U	ND	U	12.00	QJ	ND	U	ND	U	NA	
MW-4	6/3/2015	0.0052(BENTAZON)	I	ND	U	ND	U	ND	U	ND	U	NA	
MW-5	6/2/2015	ALL	U	4.00		ND	U	1.40	J	ND	U	NA	
MW-12	6/3/2015	ALL	U	1.80		ND	U	0.49	IJ	ND	U	NA	
MW-13	6/3/2015	ALL	U	0.14	T	ND	U	0.47	IJ	ND	U	NA	
MW-20	6/2/2015	ALL	U	ND	U	9.20		ND	U	ND	U	NA	
AAK7015	6/3/2015	ALL	U	0.13	T	72.00		ND	U	ND	U	NA	
BLUE SPRING (GILCHRIST)	8/26/2014	NA		0.14	T	1.00	U	0.72	IJ	ND	U	NA	
BLUE SPRING (GILCHRIST)_dup	8/26/2014	NA		0.16	T	1.00	U	0.78	IJ	ND	U	NA	
GINNIE SPRING	8/27/2014	NA		0.11	T	0.69	T	0.49	IJ	ND	U	NA	
TWIN SPRING	8/27/2014	NA		0.25	U	0.94	T	0.22	TJ	ND	U	NA	
BLUE SPRING (GILCHRIST)	6/3/2015	ALL	U	0.130	T	0.580	T	0.860	IJ	ND	U	ALL	U
DEVILS EYE SPRING	6/2/2015	ALL	U	0.230	T	ND	U	ND	U	ND	U	ALL	U
GINNIE SPRING	6/2/2015	ALL	U	ND	U	ND	U	0.370	IJ	ND	U	0.055	T
TWIN SPRING	6/2/2015	ALL	U	ND	U	ND	U	ND	U	ND	U	0.059	T
TWIN SPRING_dup	6/2/2015	ALL	U	ND	U	ND	U	ND	U	ND	U	0.100	I
SFR@47BRDG	8/25/2014	NA		0.73	I	0.84	T	0.66	IJ	ND	U	NA	
SFR@47BRDG_dup	8/25/2014	NA		0.74	I	0.87	T	0.53	IJ	ND	U	NA	
SFR@FTW USGS	8/25/2014	NA		0.69	I	0.81	T	0.47	IJ	ND	U	NA	
SFR@UP POE SPG	8/25/2014	NA		0.72	IJ	0.89	TJ	0.28	IJ	ND	U	NA	
SFR@47BRDG	10/28/2014	NA		0.66	I	0.73	T	0.62	T	ND	U	NA	
SFR@FTW USGS	10/28/2014	NA		0.53	I	0.77	T	0.62	I	ND	U	NA	
SFR@UP POE SPG	10/28/2014	NA		0.73	I	0.65	T	ND	U	ND	U	NA	
SFR@UP POE SPG_dup	10/28/2014	NA		0.62	I	0.65	T	ND	U	ND	U	NA	
SFR@47BRDG	6/2/2015	ALL	U	0.33	I	ND	U	0.52	IJ	ND	U	ND	U
SFR@FTW USGS	6/2/2015	ALL	U	0.35	I	ND	U	0.45	IJ	ND	U	ND	U
SFR@UP POE SPG	6/2/2015	ALL	U	0.38	I	ND	U	ND	U	ND	U	0.066	T
SFR@UP POE SPG_dup	6/2/2015	ALL	U	0.38	I	ND	U	ND	U	ND	U	0.045	T

Laboratory Qualifier Codes:
A – Value reported is the mean of two or more determinations.
B – Results based on colony counts outside the acceptable range.
I – The reported value is between the laboratory method detection limit and the laboratory practical quantitation limit.
J – Estimated value.
K – Actual value is known to be less than value given.
L – Actual value is known to be greater than value given.
N – Presumptive evidence of presence of material.
O – Sampled, but analysis lost or not performed.
Q – Sample held beyond normal holding time.
T – Value reported is less than the criterion of detection.
U – Material was analyzed for but not detected. The reported value is the method detection limit for the sample analyzed.
V – Analyte was detected in both sample and method blank.
X – Too few individuals to calculate SCI value.
Y – The laboratory analysis was from an unpreserved or improperly preserved sample. The data may not be accurate.
Z – Colonies were too numerous to count (TNTC).

The presence of these herbicide compounds in groundwater, springs, and river water, although in extremely low concentrations at or near laboratory detection limits, indicates their mobility and persistence in trace amounts in the subsurface from applications on cropland and other areas. With the limited number of water samples and the range in half-lives for atrazine, desethyl atrazine, and hexazinone, it is impossible to determine if the presence of these compounds originated from herbicide applications in 2014 or several years prior. It is worth noting that the reported atrazine concentrations are more than an order of magnitude lower than atrazine concentrations reported in samples from monitoring wells located throughout the UFA in Florida, Georgia, and South Carolina (Berndt et al. 2014).

Table 4. Water samples from Devil's Eye Spring with detected concentrations of pesticides, September and December 2015

ND = Not detected; Q = Qualifier code; NA = Not analyzedCompound	09/30/15 ng/L	09/30/15 Q	12/15/15 ng/L	12/15/15 Q
Atrazine	0.22	T	0.190	T
Desethyl atrazine	0.98	T	1.1	T
Dicofol	0.02	UJ	0.023	UJ
Hexazinone	0.47	T	0.500	U
Norflurazon	ND	U	0.500	U
Azinphos methyl	2.20	UJ	ND	U
Methoxychlor	ND	U	0.010	UJ

Laboratory Qualifier Codes:
A – Value reported is the mean of two or more determinations.
B – Results based on colony counts outside the acceptable range.
I – The reported value is between the laboratory method detection limit and the laboratory practical quantitation limit.
J – Estimated value.
K – Actual value is known to be less than value given.
L – Actual value is known to be greater than value given.
N – Presumptive evidence of presence of material.
O – Sampled, but analysis lost or not performed.
Q – Sample held beyond normal holding time.
T – Value reported is less than the criterion of detection.
U – Material was analyzed for but not detected. The reported value is the method detection limit for the sample analyzed.
V – Analyte was detected in both sample and method blank.
X – Too few individuals to calculate SCI value.
Y – The laboratory analysis was from an unpreserved or improperly preserved sample. The data may not be accurate.
Z – Colonies were too numerous to count (TNTC).

Implementation of Management Actions

The implementation of agricultural management actions in the RFA currently includes enrolling landowners in the FDACS BMP Program. Assessing progress to that end in the RFA involves tracking the agricultural acreage enrolled in the FDACS BMP Program over time. As illustrated in **Figure 2**, the predominant agricultural land uses in the RFA include irrigated and nonirrigated row and field crops, hay and silage, pasture, irrigated vegetables (also inventoried as row crops), and dairies, which are partially subdivided into pasture and field cropland categories.

As of December 31, 2016, 34,369 acres were enrolled under 150 NOIs, an increase of 132 NOIs since January 1, 2013. It is important to note that the number of NOIs does not correspond to the number of producers or farms. This is because a producer may sign up for one or more NOIs for different commodity types on the same acreage.

The OAWP has a statewide Implementation Assurance (IA) Program for agricultural BMPs. In mid-2016, a preliminary analysis by the OAWP indicated that at the time of BMP enrollment, most producers were already implementing 35 % to 50 % of the applicable BMPs in the Santa Fe RFA. For BMPs listed as "planned practices," the OAWP expects that they will be in place within 12 months. This schedule will be modified for BMPs that require engineering, structure, and/or cost-share support to complete.

Thirteen monitoring wells (MW1, MW2, MW3, MW4, MW7, MW9, MW11, MW12, MW13, MW15, MW16, MW18, and MW20) are located adjacent to and/or downgradient from parcels with signed NOIs as of December 31, 2016, or currently enrolled in BMPs (**Figure 25**). Nitrate-N concentrations in quarterly and semiannual samples were assessed for trends over the 4 years of the study using a Seasonal Kendall nonparametric test. **Table 7** lists the results. These trend analyses are preliminary and likely not definitive. More than 11 samples are needed to determine trends with a higher level of confidence. Most analyses for trends require a minimum of 24 samples (6 years of quarterly sampling) before a trend can definitively be assessed. For the 13 monitoring wells, 5 had statistically significant increasing trends, 4 had decreasing trends, and the remaining 4 wells showed no trend (**Table 7**).

Nitrate-N concentrations decreased in MW7 from 25 mg/L in January 2013 to 4.5 mg/L in September 2016, and decreased in MW11 from 10 mg/L to 5.3 mg/L over the same period. Both wells are located near irrigated field crops and pasture that support a dairy and are adjacent to parcels enrolled in BMPs. The dairy near MW7 was enrolled in BMPs after monitoring began. However, the dairy near MW11 was not enrolled.

The OAWP is gathering more detailed information on the timing and specific types of BMPs (such as rotational production) being implemented at agricultural sites near monitoring wells. The information was not available when this report was being prepared.

No statistically significant changes in nitrate-N concentrations were observed in water samples from the four springs or three river sites collected quarterly during the four-year study period.

This delay or lack of response in reducing N concentrations in springs or in groundwater near sites where BMPs are being implemented may be caused by one or more of the following factors:

1. Insufficient time for changes in agricultural practices to affect groundwater quality (a lag effect from when BMPs are implemented to when improvements in water quality are seen).

2. Legacy N in soil and shallow groundwater from past practices.

3. Compliance issues in the implementation of BMPs (although most of the enrollment in the RFA was from 2013 to 2015, and IA is ongoing).

4. Limitations of BMP effectiveness because of soil conditions, cropping rates, fertilization rates, and irrigation needs may warrant additional research and refinements. These may include plant tissue and soil sampling, irrigation timing and rates (using soil moisture sensors for scheduling), timing of nutrient applications, and rainfall monitoring.

The OAWP's IA Program is designed to determine the extent of BMP implementation. Also, BMPs may not be the most appropriate tool to deal with legacy nitrogen loading from past land use activities. Additional measures, such as localized projects (e.g., bioreactors for denitrification), are likely needed to address nutrient loads to groundwater and elevated nitrate concentrations at several sites.

Table 5. Agricultural BMP enrollment acreage in the Santa Fe RFA by BMP manual type and land use, as of December 31, 2016

Commodity Type	Land Use/ Land Cover Code	Code Description	Total Acres
Specialty Fruit and Nut	2100	Cropland and Pastureland	2
Specialty Fruit and Nut	2110	Improved Pastures	6
Specialty Fruit and Nut	2140	Row Crops	35
Statewide Cow/Calf	2100	Cropland and Pastureland	616
Statewide Cow/Calf	2110	Improved Pastures	5,950
Statewide Cow/Calf	2120	Unimproved Pastures	134
Statewide Cow/Calf	2130	Woodland Pastures	543
Statewide Cow/Calf	2140	Row Crops	4,029
Statewide Cow/Calf	2153	Hayfields	2,406
Statewide Cow/Calf	2410	Tree Nurseries	82
Statewide Cow/Calf	2510	Horse Farms	0
Statewide Cow/Calf	2540	Aquaculture	1
Statewide Cow/Calf	2600	Other Open Lands (Rural)	77
Statewide Cow/Calf	2610	Fallow Cropland	35
Statewide Cow/Calf	3100	Rangeland, Herbaceous (Dry Prairie)	181
Statewide Cow/Calf	3200	Shrub and Brushland	31
Statewide Cow/Calf	3300	Mixed Rangeland	83
Statewide Nurseries	2100	Cropland and Pastureland	2
Statewide Nurseries	2410	Tree Nurseries	12
Statewide Nurseries	3100	Rangeland, Herbaceous (Dry Prairie)	1
Statewide Sod	2100	Cropland and Pastureland	23
Statewide Sod	2110	Improved Pastures	0
Statewide Sod	2153	Hayfields	37
Vegetables and Agronomic Crops (2006)	2100	Cropland and Pastureland	1,443
Vegetables and Agronomic Crops (2006)	2110	Improved Pastures	5,615
Vegetables and Agronomic Crops (2006)	2120	Unimproved Pastures	132
Vegetables and Agronomic Crops (2006)	2130	Woodland Pastures	152
Vegetables and Agronomic Crops (2006)	2140	Row Crops	7,497
Vegetables and Agronomic Crops (2006)	2150	Field Crops	2
Vegetables and Agronomic Crops (2006)	2153	Hayfields	3,437
Vegetables and Agronomic Crops (2006)	2230	Other Groves (Pecan, Avocado, Coconut, Mango, etc.)	7
Vegetables and Agronomic Crops (2006)	2400	Nurseries and Vineyards	0
Vegetables and Agronomic Crops (2006)	2410	Tree Nurseries	87
Vegetables and Agronomic Crops (2006)	2430	Ornamentals	13
Vegetables and Agronomic Crops (2006)	2510	Horse Farms	0
Vegetables and Agronomic Crops (2006)	2520	Dairies	2
Vegetables and Agronomic Crops (2006)	2540	Aquaculture	1

Commodity Type	Land Use/ Land Cover Code	Code Description	Total Acres
Vegetables and Agronomic Crops (2006)	2600	Other Open Lands (Rural)	100
Vegetables and Agronomic Crops (2006)	2610	Fallow Cropland	289
Vegetables and Agronomic Crops (2006)	3100	Rangeland, Herbaceous (Dry Prairie)	220
Vegetables and Agronomic Crops (2006)	3200	Shrub and Brushland	19
Vegetables and Agronomic Crops (2006)	3300	Mixed Rangeland	194
Vegetables and Agronomic Crops (2015)	2100	Cropland and Pastureland	16
Vegetables and Agronomic Crops (2015)	2110	Improved Pastures	165
Vegetables and Agronomic Crops (2015)	2120	Unimproved Pastures	0
Vegetables and Agronomic Crops (2015)	2130	Woodland Pastures	0
Vegetables and Agronomic Crops (2015)	2140	Row Crops	416
Vegetables and Agronomic Crops (2015)	2153	Hayfields	262
Vegetables and Agronomic Crops (2015)	2510	Horse Farms	0
Vegetables and Agronomic Crops (2015)	2600	Other Open Lands (Rural)	0
Vegetables and Agronomic Crops (2015)	2610	Fallow Cropland	2
Vegetables and Agronomic Crops (2015)	3100	Rangeland, Herbaceous (Dry Prairie)	13

Table 6. Summary of NOIs to enroll in BMPs, by commodity and associated agricultural acreage in the Santa Fe RFA, as of December 31, 2016

Commodity	# NOIs	Acres
Specialty Fruit and Nut	2	43
Statewide Cow/Calf	57	14.168
Statewide Nurseries	1	15
Statewide Sod	1	60
Vegetables and Agronomic Crops	89	20,085
Total as of December 31, 2016	**150**	**34,369**

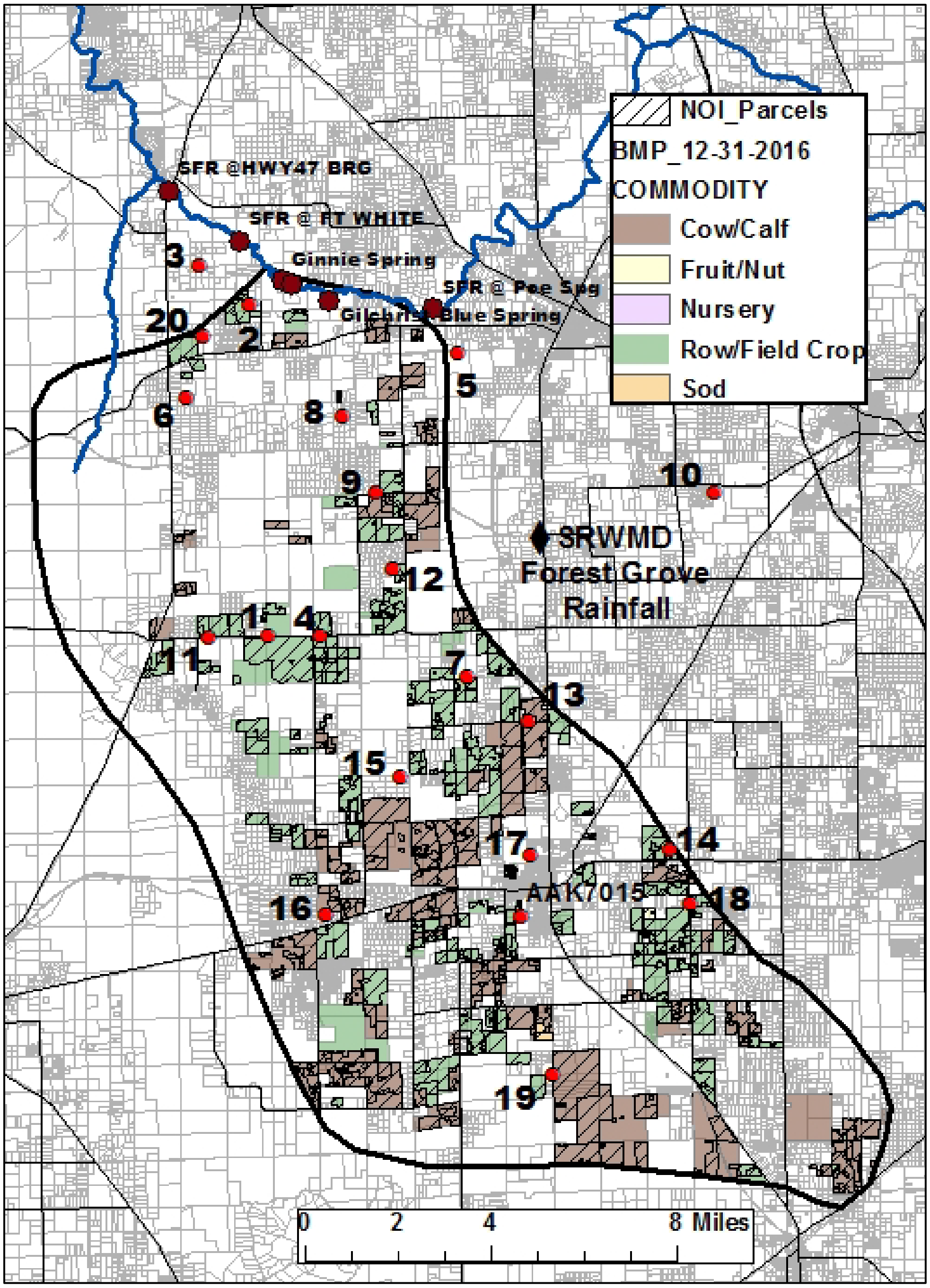

Figure 25. Map showing location of monitoring wells in relation to land parcels enrolled in agricultural BMPs by commodity in the Santa Fe RFA as of December 31, 2016 (BMP enrollment information provided by FDACS OAWP)

FDACS Disclaimer: "This map/information represents an estimate of the amount and/or location of agricultural acreage enrolled in FDACS/OAWP BMP programs for specific commodities and/or regions of the state. It is not binding, and does not otherwise affect the interest of any persons, including any vested rights or existing uses of real property. The accuracy and reliability of this map/information are not guaranteed, and are affected by continual changes in land use, crop production, and other socioeconomic factors. Due to parcel number format changes, some enrolled acreage may not be displayed."

Table 7. Results of Seasonal Kendall statistical test for trends in nitrate-N concentrations in water samples (2013–16) from monitoring wells near land parcels with NOIs to implement agricultural BMPs

* Single asterisk and red highlighting indicate increase.
** Double asterisk and green highlighting indicate decrease.

Monitoring Well Number	Nearby Land Use	BMP Status of Nearby Lands	Nitrate-N Trend	Seasonal Kendall Test p value
1	Irrigated cropland	Row crop	Increase*	0.008
2	Irrigated vegetables	Row crop	Increase*	0.008
3	Irrigated vegetables	Row crop	No change	0.47
4	Irrigated cropland	Row crop	Increase*	0.03
5	Irrigated cropland/dairy	None	No change	0.23
6	Low-density residential	None	No change	1.0
7	Irrigated field crops/pasture/dairy	Row crop	Decrease**	0.008
8	Low-density residential	None	No change	0.47
9	Pasture/nonirrigated crops	Row crop/cow-calf	Increase*	0.03
10	Irrigated cropland	None	No change	0.09
11	Irrigated field crops/pasture/dairy	Row crop	Decrease**	0.031
12	Irrigated field crops/pasture/dairy	Row crop	Increase*	0.00009
13	Irrigated cropland	Cow-calf	No change	0.089
14	Hay	None	No change	0.73
15	Irrigated cropland	Cow-calf/row crop	Decrease**	0.008
16	Irrigated cropland	Row crop	No change	0.23
17	Urban	None	No change	0.47
18	Irrigated cropland	None	Decrease**	0.03
20	Irrigated cropland	Row crop	No change	0.47
21	WWTP	None	No change	1.0

Future Sampling Schedule and Next Steps

Based on the previously discussed seasonality tests for selected groundwater quality data (nitrate-N, potassium, sulfate, and dissolved solids), the sampling schedule was modified in mid-2015 to reduce the sampling frequency of the RFA monitoring wells from quarterly to semiannually, except for MW12. This well with high nitrate-N concentrations (consistently exceeding 40 mg/L) is located near an agricultural site with an experimental groundwater remediation system, which includes several scavenger wells that pump groundwater into a bioreactor designed to reduce nitrate-N concentrations in groundwater. The sampling of most of the existing network of monitoring wells will continue semiannually.

Quarterly sampling will continue for the four RFA springs (Ginnie, Gilchrist Blue, Twin, and Devil's Eye) and the three Santa Fe River sites. Water quality trend analyses will continue as additional data are collected from future sampling events. Nitrate and other water quality data will continue to be evaluated regularly, and sampling frequency will be adjusted as needed in future events based on the results. For example, if there are substantial changes in land use, rainfall, nitrate-N concentrations, or BMPs, the sampling frequency of all impacted monitoring wells would revert to quarterly.

The continuous monitoring station at Ginnie Spring will be maintained through 2017 by a DEP contractor, although the SUNA nitrate sensor will be offline for several months for servicing.

In addition to the implementation of agricultural BMPs, FDACS, the SRWMD, and DEP will continue to review results from the experimental bioremediation system, which consists of a network of scavenger wells and a bioreactor to remove N from recovered groundwater beneath an agricultural property with elevated groundwater nitrate-N concentrations. Because of early positive results from this experimental site, other "pump and treat" systems based on this design have been deployed at other agricultural sites in the state.

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Appendices

Appendix 1. List of Analytes in Water Samples from Wells, Springs, and River Sites in the Santa Fe RFA Monitoring Network

mg/L = Milligrams per liter; TDS = Total dissolved solids; TSS = Total suspended solids; mg N/L = Milligrams per liter of nitrogen; mg P/L = Milligrams per liter of phosphorus; µg/L = Micrograms per liter; Ortho-P = Orthophosphate; Total-P = Total phosphorus; ppt = parts per thousand (‰)

Chemical Indicators	Unit	Laboratory (L) or Field (F) Analysis Method	Justification
Alkalinity	mg $CaCO_3$/L	SM 2320 B (L)	Aquifer properties
Chloride	mg/L	Method 300 (L)	Source indicator
Fluoride	mg/L	SM 4500 F-C (L)	Confinement indicator
Sulfate	mg/L	Method 300 (L)	Source indicator
TDS	mg/L	SM 2540 C (L)	Source indicator
TSS	mg/L	SM 2540 D (L)	Source indicator
Bromide	mg/L		Source indicator
Boron	mg/L		Source indicator
Calcium	mg/L	Method 200.7 (L)	Aquifer properties
Magnesium	mg/L	Method 200.7 (L)	Aquifer properties
Potassium	mg/L	Method 200.7 (L)	Source indicator
Sodium	mg/L	Method 200.7 (L)	Source indicator
Ammonia-N	mg N/L	Method 350.1 (L)	Source indicator/ aquifer properties
Nitrate-Nitrite-N	mg N/L	Method 353.2	Management action influence; source indicator/nitrogen species transformation
Total-P	mg P/L	In-house based on Method 365.4 (L)	Aquifer properties; Hawthorne influence
Total Kjeldahl Nitrogen	mg N/L	In-house based on Method 351.2 (L)	Source indicator/ nitrogen species transformation
Organic Carbon	mg C/L	In-house based on Method 415.1 (L)	Aquifer properties
Ortho-P	mg P/L	Method 365.1 (L)	Aquifer properties; Hawthorne influence
Sucralose	µg/L	In-house	Source indicator
Nitrogen and Oxygen Isotopes in nitrate (δ15N and δ18O in NO_3)	ppt	Colorado Plateau Stable Isotope Laboratory	Nitrate-N source indicator; denitrification indictor

Appendix 2. List of Field-Measured Physical and Chemical Indicators for Groundwater, Springs, and River Water Sites in the Santa Fe RFA Monitoring Network

DO = Dissolved oxygen; mg/L = Milligrams per liter; SU = Standard units; µS/cm = Micromhos per centimeter;
NTU = Nephelometric turbidity units; PCU = Platinum cobalt units; °C = Degrees Celsius; ft = feet

Physical Indicators	Unit	Analysis Method	Justification
DO	mg/L	DEP-SOP-001/01 FT 1500 (F)	Aquifer properties/ redox conditions
pH	su	DEP-SOP-001/01 FT 1100 (F)	Aquifer properties
Specific Conductance	µS/cm	DEP-SOP-001/01 FT 1200 (F)	Aquifer properties
Turbidity	NTU	Method 180.1 (L)	Aquifer properties
Color	PCU	SM 2120 B (L)	Aquifer properties
Temperature	°C	DEP-SOP-001/01 FT 1400 (F)	Aquifer properties
Depth to Water (wells)	ft	Field Measurement	Recharge to aquifer

Appendix 3. Santa Fe RFA Water Quality Data, 2013–16

Spreadsheet containing water quality data for 2013 to 2016 is available on request.

Appendix 4. List of Pesticide Compounds Analyzed by the DEP Laboratory Along with Their Detection Limits

DEP SOP: GC-011-5 (based on EPA 608 and 617)

ug/L = Micrograms per liter

Pesticide	Detection Limit	Unit of Measurement
Aldrin	0.0019	µg/L
Alpha-BHC	0.0019	µg/L
Beta-BHC	0.0019	µg/L
Delta-BHC	0.0019	µg/L
Gamma-BHC	0.0019	µg/L
Carbophenothion	0.0057	µg/L
Chlorothalonil	0.0076	µg/L
Cypermethrin	0.011	µg/L
DDD-p,p	0.0038	µg/L
DDE-p,p	0.0038	µg/L
DDT-p,p	0.0038	µg/L
Dicofol	0.023	µg/L
Endosulfan I	0.0019	µg/L
Endosulfan II	0.0019	µg/L
Endosulfan Sulfate	0.0038	µg/L
Endrin	0.0038	µg/L
Endrin Aldehyde	0.0038	µg/L
Heptachlor	0.0019	µg/L
Heptachlor Epoxide	0.0019	µg/L
Methoxychlor	0.0095	µg/L
Mirex	0.0038	µg/L
Permethrin	0.0095	µg/L
Trifluralin	0.0076	µg/L

DEP SOP: LC-001-2 (based on USGS O-2060-01)

ug/L = Micrograms per liter

Pesticide	Detection Limit	Unit of Measurement
2,4-D	0.0020	µg/L
Diuron	0.0020	µg/L
Fenuron	0.0080	µg/L
2,4,5-T	0.0020	µg/L
Acifluorfen	0.0020	µg/L
Imidacloprid	0.0020	µg/L
Bentazon	0.0020	µg/L
Linuron	0.0040	µg/L
Silvex	0.0020	µg/L

EPA 8321B

ug/L = Micrograms per liter

Compound	Detection Limit	Unit of Measurement
Sucralose	0.010	µg/L
2,4-D	0.0020	µg/L
Diuron	0.0020	µg/L
2,4-DB	0.0020	µg/L
Fenuron	0.0040	µg/L
2,4,5-T	0.0020	µg/L
Acifluorfen	0.0020	µg/L
Imidacloprid	0.0020	µg/L
Bentazon	0.0020	µg/L
Linuron	0.0040	µg/L
Dichlorprop	0.0020	µg/L
Dinoseb	0.020	µg/L
MCPA	0.0040	µg/L
MCPP	0.0040	µg/L
Silvex	0.0020	µg/L

EPA 8270D

ng/L = Nanograms per liter

Compound	Detection Limit	Unit of Measurement
Dieldrin	0.38	ng/L
Ametryn	0.19	ng/L
Atrazine	0.24	ng/L
Chlorpyrifos Ethyl	0.097	ng/L
Chlorpyrifos Methyl	0.12	ng/L
Disulfoton	0.49	ng/L
Ethion	0.097	ng/L
Ethoprop	0.097	ng/L
Hexazinone	0.97	ng/L
Malathion	0.12	ng/L
Metribuzin	0.24	ng/L
Mevinphos	0.24	ng/L
Norflurazon	0.97	ng/L
Phorate	0.24	ng/L
Prometryn	0.24	ng/L
Simazine**	0.24	ng/L
Atrazine Desethyl	0.24	ng/L
Fipronil	0.49	ng/L
Molinate	0.29	ng/L
Pendimethalin	0.49	ng/L
Terbufos	0.097	ng/L
EPTC	0.29	ng/L
Terbuthylazine	0.19	ng/L
Bromacil	0.49	ng/L
Fipronil Sulfide	0.19	ng/L
Fipronil Sulfone	0.19	ng/L

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ng/L = Nanograms per liter

Compound	Detection Limit	Unit of Measurement
Ametryn	0.19	ng/L
Atrazine	0.24	ng/L
Chlorpyrifos Ethyl	0.097	ng/L
Chlorpyrifos Methyl	0.12	ng/L
Disulfoton	0.49	ng/L
Ethion	0.097	ng/L
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Pendimethalin	0.49	ng/L
Terbufos	0.097	ng/L
EPTC	0.29	ng/L
Terbuthylazine	0.19	ng/L
Bromacil	0.49	ng/L
Fipronil Sulfide	0.19	ng/L
Fipronil Sulfone	0.19	ng/L