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Discrimination of Nitrogen Sources in Karst Spring Contributing Areas Using a Bayesian Isotope Mixing Model and Wastewater Tracers (Florida, USA)

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ABSTRACT

Many springs in Florida have experienced a proliferation of nuisance algae and alteration of trophic structure in response to increases in nitrate concentration concurrent with rapid population growth and land use intensification beginning in the mid-20th century. While loading targets and remediation plans have been developed by state agencies to address excess nitrogen inputs, further confirmation of the relative contribution of nitrogen sources to groundwater is necessary to optimize the use of resources when implementing projects to reduce nitrogen loads. In the present study, stable isotopes of nitrate and wastewater indicators were used to discriminate sources of nitrogen in wells and springs in central Florida. Sampling was performed in 50 wells at 38 sites and at 10 springs with varying levels of agriculture and urban development. Nitrate isotope values were used to develop Bayesian mixing models to estimate the probability distribution of the contributions of nitrate sources in wells. Prior probabilities for the fractional contribution of each source were adjusted based on land use and density of septic tanks. Sucralose and the Cl:Br mass ratio were used as confirmatory indicators of wastewater sources. In residential areas, mixing model results indicated that fertilizer or mixed fertilizer and wastewater (septic tank effluent and reuse water) were the primary sources, with sucralose detections corresponding to wells with elevated contributions from wastewater. Sources of nitrogen in pasture and field crop areas were primarily fertilizer and manure; however, model posterior distributions of $\delta^{15}N$ indicated that manure sources may have been overpredicted. The present study demonstrates the utility of a multi-tracer approach to build multiple lines of evidence to develop locally relevant remediation strategies for nitrogen sources in groundwater.

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INTRODUCTION

Florida has over 700 documented springs, the majority of which are karst springs fed by the Floridan Aquifer System (Scott et al., 2004). Florida's springs are concentrated in the northwest and north-central areas of the state and contribute significant flows to river systems in these areas. Many of these springs have experienced varying levels of ecosystem degradation in response to anthropogenic stressors. The most widely observed impact in spring systems is the proliferation of epiphytic and benthic algae, which has been attributed primarily to increases in nitrate concentrations at spring vents (Stevenson et al., 2007; Quinlan et al., 2008). Across Florida springs, nitrate-N concentrations have risen from pre-development values of less than 0.1 mg L^{-1} to present day values of between 0.5 and 5.0 mg L^{-1}, with nitrate-N concentrations in some small springs exceeding 30 mg L^{-1} (Katz, 1992; Katz et al., 1999). In response to the impact of elevated nitrate at springs, the state of Florida established a numeric nutrient criterion that nitrate plus nitrite not exceed 0.35 mg L^{-1} at spring vents (Fla. Admin. Code R. 62-302.531), based on limiting concentrations for algal growth.

Determining the relative contribution and locations of nitrogen sources to groundwater within springs contributing areas (springsheds) is critical for planning of cost-effective reduction of nitrogen loading to springs and downstream water bodies. Previous work has established springshed-scale nitrogen budgets using a combination of land use, specific source data (e.g., septic tanks, wastewater application), hydrogeologic data, and nitrogen attenuation factors based on literature reports (Katz et al., 2009; Tucker and Stroehlen, 2010; and Eller and Katz, 2017). Although these approaches provide spatially explicit estimates of nitrogen sources and loads at the land surface and top of aquifer, they have limited ability to account for spatial heterogeneity in soil biogeochemical transformations, aquifer transport, and attenuation by aquifer denitrification. Given that large springsheds may range in size from hundreds to thousands of square kilometers, further spatial refinement of groundwater impacts may be accomplished using geospatial and statistical models to predict groundwater nitrate concentrations, which implicitly account for spatial heterogeneity (Nolan et al., 2002; Almasri and Kaluarachchi, 2007; and Canion et al., 2019). Further discrimination of differential transport and attenuation of nitrogen sources may be accomplished using geochemical tracers. This approach is often desirable where heterogeneous land use and multiple nitrogen sources impact groundwater.

The most widely used method for determining nitrate sources in groundwater is the dual isotope approach, where the isotopic ratios of nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) are measured simultaneously in nitrate (Xue et al., 2009). Because of differences in source isotopic ratios, this approach may be used to quantify, based on mass balance, nitrate contributions from atmospheric deposition, nitrate fertilizer, ammonia/organic nitrogen fertilizer, natural soil organic matter, wastewater, and manure (Kendall et al., 2008). However, the dual isotope approach still has limitations for identification and quantification of sources. Assumptions must be made about the extent of isotopic overprinting by biogeochemical cycling in the soil and aquifer (Kendall et al., 2008), and quantification by linear mixing models is complicated by significant overlap in the distributions of source isotopic values and undetermined systems ($>n + 1$ sources, where n is the number of isotope tracers). Statistical summaries that provide a range of solutions were proposed by Phillips and Gregg (2003) in order to overcome scenarios where no unique mixing model solution existed.

Recently, the incorporation of a Bayesian framework into isotope mixing models has furthered statistical estimation of nitrate sources by incorporating variation in source isotopic values and prior information on source contribution. The SIAR (Stable Isotope Analysis in R) Bayesian mixing model (Parnell et al., 2010) has been applied in agriculturally-dominated watersheds in Belgium and France to determine contributions from fertilizer, manure, and wastewater to springs and surface water (Xue et al., 2012; El Gaouzi et al., 2013). The SIAR model was also recently applied to stormwater runoff data from residential catchments in Florida, where it was determined that atmospheric deposition and synthetic fertilizers were the primary sources of nitrate (Yang and Toor, 2016). Ransom et al. (2016) used a Bayesian framework with two additional tracers ($\delta^{11}B$ and iodine concentration) to discriminate septic tank, manure, and fertilizer nitrogen sources in shallow domestic wells in the Central Valley in California, and source contributions were validated by an analysis of surrounding land use. Unlike SIAR, the Central Valley model was able to assign non-normal prior distributions for source isotopic ratios.

Additional geochemical markers may also be used to supplement nitrate stable isotopes in determining groundwater nitrogen sources. Boron stable isotope measurements ($\delta^{11}B$) have been used to improve discrimination between wastewater and animal manure sources (Vengosh, 1998; Widory et al., 2004, 2005). The ratio of chloride to bromide, along with chloride concentration, was shown to be a marker for septic tank nitrogen inputs in multiple aquifers in the United States (Katz et al., 2011). A number of wastewater organic microconstituents have also been evaluated as conservative, co-migrating tracers of nitrogen (Badruzzaman et al., 2013). Of these organic tracers, sucralose has been identified as one of the most conservative because it is highly soluble, has low rates of microbial degradation (half-life ~1 year), and has low potential sorption to soils (Oppenheimer et al., 2011; Soh et al., 2011). Statewide surveys in Florida have seen high detection rates for sucralose, indicating its usefulness as a widespread wastewater tracer in surface and groundwater (Silvanima et al., 2018). Sucralose does not, however, discriminate between septic tank nitrogen sources and land-applied treated wastewater (reuse); therefore, tracers unique to wastewater treatment facilities, including gadolinium anomaly and iohexol, have been proposed to further discriminate between wastewater sources (Schmidt et al., 2013).

Although land surface nitrogen load targets have been developed to address excess nitrogen loading to many springs in Florida, further confirmation of the relative contribution of local nitrogen sources to groundwater is necessary to optimize the use of resources when implementing projects to reduce nitrogen loads. In the present study, stable isotopes of nitrate and wastewater indicators were used to discriminate local sources of nitrogen in wells and springs in central Florida. A Bayesian mixing model was fit to the dual

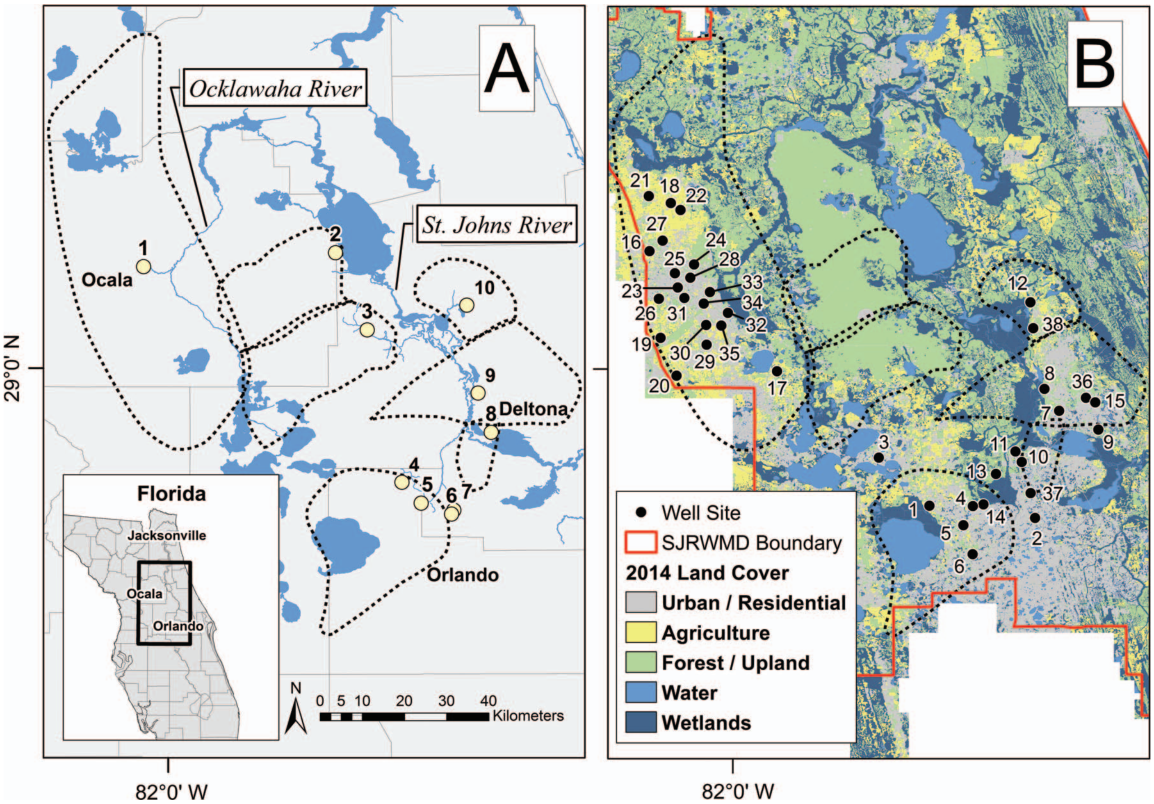

Figure 1. (A) Location of springs sampled: (1) Silver Springs, (2) Silver Glen Springs, (3) Alexander Springs, (4) Rock Springs, (5) Wekiva Springs, (6) Sanlando Spring, (7) Starbuck Spring, (8) Gemini Springs, (9) Blue Spring, (10) Ponce DeLeon Springs. Dashed lines indicate contributing areas based on the Upper Floridan Aquifer potentiometric surface. (B) Well sites (corresponding to Table 3) and land use (2014) in the study area. The St. Johns River Water Management District (SJRWMD) boundary is shown in red.

nitrate isotope data from wells using the JAGS software (Plummer, 2017), based on the methods described by Ransom et al. (2016). Land use data were applied to set informative prior distributions on the nitrate source contributions to wells in the mixing models. Analysis of wastewater indicators provided additional evidence for contributions of wastewater nitrogen. In wells with only reduced nitrogen or where denitrification had occurred, the mixing model could not be applied, and wastewater indicators provided an alternative indicator of nitrogen source.

STUDY AREA AND METHODS

Study Area

The area of study was in central Florida along the middle St. Johns and Ocklawaha rivers (Figure 1), an area characterized by mantled karst topography. These two river valleys lie between ridges with sandy soils and high recharge potential, and significant groundwater inputs to the rivers from artesian Upper Floridan Aquifer springs as well as diffuse groundwater flow occur in this region (Belaineh et al., 2012). The Upper Floridan Aquifer is highly permeable in most places and includes the Ocala Limestone and Avon Park formations, where transmissivity values are between 900 and 9,000 m^2 d^{-1} (Kuniansky et al., 2012). The Upper Floridan Aquifer is mostly unconfined in the northwestern parts of the study area (near Silver Springs) and is semi-confined to confined by the intermediate confining unit, comprised of Miocene Hawthorn Group clays, in the southern and eastern parts of the study area. In confined areas, a surficial aquifer is present that is capable of recharging to the Upper Floridan Aquifer due to leakance and solution features (Boniol et al., 1993).

Four first-magnitude springs (>2.8 m^3 s^{-1} discharge), six second-magnitude springs (>0.28 m^3 s^{-1} discharge), and 50 wells within contributing areas (springsheds) were selected for study (Table 1). The wells sampled withdraw water from the Upper Floridan Aquifer (33 wells), producing zones within the intermediate confining unit (intermediate aquifer, five wells), and the surficial aquifer (12 wells). Dominant land use between the springsheds is varied, including forested, urban/residential, and mixed urban/residential and agriculture. Additionally, some

Table 1. *Hydrologic characteristics of springs and land cover of contributing areas.*[1]

Spring	Estimated Springshed Area (km^2)	Average Discharge ($m^3\ s^{-1}$)	Apparent Age[2] (yr)	Chemistry Type	Agriculture (%)	Urban and Residential (%)	Forest, Water, Wetlands (%)	Total Septic Tanks
Alexander Springs	620	3.0	24.7	Na-Cl	8	6	86	7,200
Blue Spring	636	4.2	22.2	Na-Cl	7	28	65	51,400
Gemini Springs	110	0.3	<5	Na-Cl	3	52	45	4,600
Ponce De Leon Springs	263	0.8	21.7	Na-Cl/Ca-HCO_3	17	9	74	4,400
Rock Springs	741[3]	1.7	21.3	Ca-HCO_3	9	39	52	39,300
Sanlando Spring	80[4]	0.5	22.8	Ca-HCO_3	0	77	23	7,600
Silver Glen Springs	491	3.0	26.1	Na-Cl	1	5	94	4,400
Silver Springs	2,324	21.7	34.5	Ca-HCO_3	23	21	56	63,000
Starbuck Spring	80[4]	0.4	19.1	Ca-HCO_3	0	73	27	8,000
Wekiwa Springs	741[3]	1.9	13.5	Ca-HCO_3	9	39	52	39,300

[1]Land cover percentages are from the 2014 Land Use/Land Cover map (SJRWMD, 2018). Total septic tanks are from the Florida Water Management Inventory Project (FDOH, 2016).
[2]Based on $^3H/^3He$ (Toth and Katz, 2006; Walsh, 2009; and Knowles et al., 2010).
[3]Wekiwa and Rock Springs delineated as a combined springshed.
[4]Approximated based on a 5-km-radius circular buffer; size chosen based on ratio of springshed area to discharge at Wekiva Springs.

springsheds have a high percentage of developed areas with septic tanks (Florida Department of Health [FDOH], 2016). The springs vary in major ion composition, with springs near the St. Johns River having a Na-Cl water type due to relict (or residual connate water) seawater inputs and springs farther from the St. Johns River having a Ca-HCO_3 water type consistent with dissolution of limestone that forms the Upper Floridan Aquifer. The apparent water age of all study springs is young, ranging from less than 5 years old to 36 years old (Table 1). Previous work has demonstrated that apparent ages in these springs is a result of mixing of 30%–70% recently recharged water ($<$10 years) with older ($>$60 years) water (Toth and Katz, 2006).

Sampling and Analytical Methods

Sampling at the springs and wells occurred between February and July 2018 and was performed in accordance with Florida Department of Environmental Protection (FDEP) standard protocols. Field measurements of conductivity and dissolved oxygen were recorded at the time of sampling. Samples collected for nitrate dual isotope analysis were filtered through a 0.45-μm filter into high-density polyethylene bottles at the time of sampling and frozen until analysis. Samples for sucralose and iohexol were collected unfiltered in glass containers (amber glass for iohexol) and refrigerated until analysis.

Nitrogen species, chloride, and bromide were analyzed at the St. Johns River Water Management District (SJRWMD) using analytical methods approved by the U.S. Environmental Protection Agency. Method detection limits for NO_3^-, NH_4^+, and TKN, were 0.01, 0.005, and 0.05 mg L^{-1}, respectively. Chloride and bromide had detection limits of 3 mg L^{-1} and 0.1 mg L^{-1}, respectively. Analysis of $\delta^{15}N$ and $\delta^{18}O$ of nitrate was performed at the University of California at Davis Stable Isotope Facility using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Reference standards for $\delta^{15}N$ and $\delta^{18}O$ were air and Vienna Standard Mean Ocean Water, respectively, and accepted analytical precision was 0.4‰ for $\delta^{15}N$ and 0.5‰ for $\delta^{18}O$. Sucralose was analyzed via high-performance liquid chromatography/tandem mass spectrometry (LC-MS/MS) at the FDEP Central Laboratory (Tallahassee, FL) using the methods described in Silvanima et al. (2018). The method detection limit for sucralose was 10 ng L^{-1}. Iohexol was analyzed by Eurofins Eaton Analytical (Monrovia, CA) with solid phase extraction followed by LC-MS/MS. The minimum reporting level for iohexol was 100 ng L^{-1}.

Land Use and Wastewater Nitrogen Sources

Land use surrounding each monitoring well was calculated from the St. Johns River Water Management District 2014 Land Cover/Land Use spatial layer (SJRWMD, 2018). Land use polygons were clipped in a 1-km-radius circular buffer using ArcGIS 10.6.1. Polygon areas were aggregated based on the highest level (level 1) of the Florida Land Use, Cover and Forms Classification System to calculate the percentage of each land use category. To confirm whether changes in the dominant land use surrounding a well had occurred, a 1989 land use layer from SJRWMD was analyzed using the same buffers as the 2014 land use. The land use with the largest area within the buffer was compared between 1989 and 2014.

Wastewater sources to groundwater were not captured by land use coverages, and thus the proximity of wastewater-derived sources to groundwater was determined using other spatial data sets. Septic tank locations were derived from a parcel-based model developed by the FDOH (2016). In each buffer area used for land use analysis, the centroids were calculated for parcels classified as having a septic tank. The total number of septic tanks was then calculated for each buffer area. Application of treated wastewater (reuse water) for irrigation and recharge is a highly utilized strategy for water conservation in central Florida. Due to difficulties in accurately determining the quantities of water reuse application at spatial scales relevant to this study, a qualitative analysis was used to determine reuse application within well buffer areas. A spatial data set with reuse water service lines and destination areas (SJRWMD, unpublished) was overlaid with the 1-km-radius well buffers to determine the presence and type of reuse. Three types of reuse water locations were identified: (1) residential irrigation, (2) golf course irrigation, and (3) direct application of reuse (e.g., wastewater sprayfields, rapid infiltration basins, percolation ponds). The source reuse water was expected to have similar chemical composition, but the reuse locations varied in timing and intensity of water application and have variable capacity for nitrogen attenuation in the soil zone.

Bayesian Mixing Model

A Bayesian mixing model was developed with the nitrate isotope values ($\delta^{15}N$, $\delta^{18}O$) as tracers and four sources of nitrate, including wastewater (septic tank effluent and reuse water), manure, NO_3^- fertilizer, and NH_4^+ fertilizer (includes synthetic organic nitrogen fertilizer). Atmospheric deposition of nitrogen was not included based on the observation that $\delta^{18}O$ values indicated minimal atmospheric deposition contribution. Nitrogen from naturally occurring organic matter in soils was likewise excluded from the analysis based on the rationale that all the wells chosen for study had elevated nitrogen from anthropogenic sources. Also, most soils in the study area contain low amounts of organic matter. Background nitrate concentrations in Floridan Aquifer water are generally less than 0.1 mg L^{-1} (Katz, 1992; Cohen et al., 2007), and thus natural soil organic nitrogen is expected to contribute minimally to wells sampled in the present study. Wells with evidence of denitrification were excluded from the analysis. A threshold concentration of 0.5 mg L^{-1} dissolved oxygen was used to exclude wells where significant denitrification had occurred. After removal of wells with presumed denitrification, a total of 31 wells were selected for analysis in the mixing model.

The mixing model was based on two mass balance equations from Ransom et al. (2016) and initially from Accoe et al. (2008) where each measured isotope value was modeled as a linear combination of the fractional contribution of each source of nitrate to the well multiplied by the isotopic signature of each corresponding source:

$$\delta^{15}N_{\text{mixture}} = \sum\nolimits_{\text{source}=1}^{4} f_{\text{source}} * \delta^{15}N_{\text{source}} + \varepsilon_N \quad (1)$$

$$\delta^{18}O_{\text{mixture}} = \sum\nolimits_{\text{source}=1}^{4} f_{\text{source}} * \delta^{18}O_{\text{source}} + \varepsilon_O \quad (2)$$

where ε is a Gaussian error term reflecting stochastic variation in the isotope value and is unique to each well. For use in the model, the mass balance equations were combined into matrix form. The matrix form of the mixing model initially comes from Massoudieh and Kayhanian (2013) and is written as

$$C = YF + E \quad (3)$$

where C is a 2-by-31 matrix of two measured isotope values in 31 wells, Y is a 2-by-4 matrix of two isotopic signatures in four sources, F is a 4-by-31 matrix of four fractional source contributions to each of the 31 wells, and E is a 2-by-31 matrix of errors for each tracer in each well. A Dirichlet distribution was used as the prior distribution for the fractional contributions of each source of nitrate to each well. The Dirichlet distribution is a multivariate generalization of the beta distribution for K classes (K = 4 sources) and ensures that the fractional source contributions from each well will sum to one.

Informative prior means for the fractional contributions of wastewater and manure were set for each well based on land use and the number of septic tanks in a 1-km radius (Appendix, Table A1). The Dirichlet parameter, α, was adjusted where there was less prior evidence for either wastewater or manure sources. The resulting prior mean fractional contribution for each source is calculated as

$$\mu_{\text{source}} = \frac{\alpha_{\text{source}}}{\sum_{\text{source}=1}^{4} \alpha_{\text{source}}} \quad (4)$$

The wastewater source α prior was adjusted according to the following rules for the percentage of urban land use with a given number of septic tanks:

a. 1/5 for ≤ 20% urban land use with ≤ 100 septic tanks
b. 1/2 for ≥ 20% urban land use with ≤ 100 septic tanks
c. 1 for ≥ 20% urban land use with ≥ 100 septic tanks

Similarly, the manure source α prior was adjusted based on the percentage of agricultural land use according to the following rules:

a. 1/10 for < 1% agricultural land use
b. 1/5 for 1%–10% agricultural land use
c. 1/2 for 10%–20% agricultural land use
d. 1 for > 20% agricultural land use

Dirichlet priors for fertilizer sources were not adjusted based on land use because fertilizer application occurs at both agricultural and residential sites and because limited information on the relative use of nitrate versus ammonium/organic fertilizers was available. The alpha parameters were assigned to the Dirichlet distribution for each fractional source contribution of nitrate to each well in order to achieve the desired informative prior mean and relatively low prior variance. Low prior variance assisted model convergence and required strong evidence of the isotopic measurements to move the posterior fractional source contribution distributions away from the priors.

Literature values were compiled to establish empirical prior distributions for each combination of tracer and source (Appendix, Table A2). Prior distributions were fit using the fitdistrplus and MASS packages within the R statistical computing environment (Delignette-Muller et al., 2019; R Core Team, 2019; and Ripley et al., 2019). A gamma or a Student t distribution was used as the prior distribution for the $\delta^{15}N$ and $\delta^{18}O$ source signatures. The gamma distribution was chosen for $\delta^{15}N$ in manure and wastewater, as the isotopic $\delta^{15}N$ values in these two sources are unlikely to be negative and the distributions tend to be right-skewed. We chose not to include the dairy manure source $\delta^{15}N$ values referenced in Ransom et al. (2016) because the livestock in the present study area were almost entirely beef cattle and horses. This led to a lower mean $\delta^{15}N$ value for the manure source, which more accurately reflects lower ammonia volatilization and lower isotopic enrichment associated with pasture applied and stockpiled manure. Prior distributions for $\delta^{15}N$ in NO_3^- and NH_4^+ fertilizer, as wells as prior distributions for all $\delta^{18}O$ source values, were fit using a Student t distribution with 10 degrees of freedom. A Gaussian distribution was chosen as the likelihood distribution to represent Eq. 3. The choice of the Gaussian distribution ensured the real space, linear combination of isotopic values from each of the four sources as described in Eqs. 1 and 2.

Markov chain Monte Carlo methods were used to estimate the posterior probability distribution of each of the four sources' fractional contribution of nitrate to each well. Analysis was performed with the Gibbs sampler JAGS (Plummer, 2017) within the R statistical computing environment (R Core Team, 2019) using the package rjags (Plummer, 2018). We used an adaptation and burn-in phase of 2 million iterations for each of two chains. The sampling phase consisted of 50,000 samples with a thinning rate of 100 for a total of 500 posterior realizations retained from each chain. Finally, the posterior realizations from each chain were combined for each monitored parameter. The final model run took approximately 2 hours on an Intel Xeon E3-1505M chipset running at 3.00 GHz with 32 GB of ECC DDR4 RAM at 2,400 MHz. Trace, autocorrelation, running mean, and density plots were visually inspected for model convergence and proper mixing of chains. Normalized central tendencies were calculated for each set of four fractional source contributions for each well as a summary measure of the likely proportional contribution of each source to each well. Normalized central tendencies were calculated as the geometric mean of each posterior distribution of fractional source contributions, normalized by well.

RESULTS AND DISCUSSION

Nitrogen Forms and Concentrations

Nitrogen in Spring Vents

Nitrate-N concentrations in springs ranged from 0.04 to 0.05 mg L^{-1} in springs with unimpacted, forested watersheds (Alexander Springs, Silver Glen Springs) up to 0.39–1.4 mg L^{-1} for the remainder of springs (Table 2). The range of nitrate-N for the current study springs, which have springsheds influenced primarily by urban and residential land use, is lower than a previously reported range of 1.0–4.2 mg L^{-1} for Florida springs with predominantly agricultural land use (Katz, 2004). It is important to note that some of the difference in nitrate concentrations between the current study springs with residential land use and previous results from springs in agricultural areas may be due to regional differences in aquifer geochemistry. Previous work by Heffernan et al. (2012) in Florida springs found significant denitrification (35%–90% N removal) in all of the current study springs based on dissolved gas and other chemical data (Table 2), whereas the agriculturally influenced springs studied by Katz (2004) were found to have less nitrogen removed by denitrification (0%–40%). This difference in denitrification is most likely due to a lack of confinement of the Upper Floridan Aquifer and oxic conditions in the agriculturally influenced springs, whereas in all the current study springs except Silver Springs, some degree of confinement was present within their springsheds, allowing for the development of low dissolved oxygen and subsequent denitrification.

Table 2. *Water quality parameters and source indicators at springs.*

Site	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	TKN (mg L^{-1})	$\delta^{15}N$-$NO_{3\,Air}$ (‰)	$\delta^{18}O$-$NO_{3\,VSMOW}$ (‰)[1]	Dissolved Oxygen (mg L^{-1})	Percent of Nitrogen Remaining[2]	Sucralose (ng L^{-1})	Cl:Br	Iohexol (ng L^{-1})
Alexander Springs	0.04	0.01	0.05	8.01	2.34	1.9	12%	ND[3]	331	ND
Blue Spring	0.79	ND	0.07	11.82	6.95	1.4	13%	320	304	ND
Gemini Springs	1.40	0.03	0.10	7.09	4.28	1.0	50%–65%	330	345	ND
Ponce De Leon Springs	0.81	0.04	0.10	9.80	9.54	1.1	21%–31%	130	290	ND
Rock Springs	1.28	ND	0.04	6.60	8.08	1.0	43%	160	270	ND
Sanlando Spring	0.62	0.11	0.20	14.88	10.39	0.6	10%	960	371	ND
Silver Glen Springs	0.05	0.01	ND	5.43	− 0.39	3.6	11%	ND	340	ND
Silver Springs	1.24	0.01	0.08	7.30	5.74	2.3	50%–93%	36	327	ND
Starbuck Spring	0.39	0.04	0.06	19.99	8.91	0.8	10%	460	341	ND
Wekiwa Springs	1.12	ND	0.08	11.49	9.67	0.5	30%	870	360	ND

[1]VSMOW = Vienna Standard Mean Ocean Water.
[2]Data from Heffernan et al. (2012).
[3]ND = not detected.

Reduced forms of nitrogen were also present at spring vents but were significantly lower than nitrate. Total Kjeldahl nitrogen (TKN) concentrations were between 0.04 and 0.2 mg L^{-1}, and ammonium-N concentrations were between 0 and 0.11 mg L^{-1}. The presence of reduced forms of nitrogen may be an indication of (1) assimilatory nitrate reduction and dissimilatory nitrogen reduction to ammonium (DNRA) in reducing areas of the surficial and Upper Floridan aquifers or (2) mixing of deep Upper Floridan and Lower Floridan water with shallow upper Floridan water (Toth and Katz, 2006; Knowles et al., 2010). Recently, *in situ* push-pull tracer experiments provided rate estimates and microbial functional gene evidence for DNRA as a significant nitrate reduction pathway in the Upper Floridan Aquifer that co-occurs with denitrification (Henson et al., 2017). An analysis of deeper, Lower Floridan Aquifer wells in the study area revealed consistently higher ammonia concentrations (0.30 ± 0.28 mg L^{-1} NH_4-N) than nitrate concentrations (0.01 ± 0.003 mg L^{-1}), indicating the DNRA may be a significant nitrate reduction pathway in the deeper groundwater that mixes with more recently recharged water (n = 10; SJRWMD unpublished data).

Nitrogen in Wells

Surficial and intermediate groundwater well NO_3-N concentrations were generally low and ranged from 0.01 to 1.32 mg L^{-1}, with a median value of 0.06 mg L^{-1}. In Upper Floridan wells, NO_3-N exhibited two patterns dependent on the springshed where they were located (Table 3). Median concentrations of NO_3-N were 1.87 mg L^{-1} in wells from the Silver Springs springshed and <0.01 mg L^{-1} all other springsheds. For the Silver Springs springshed, NO_3-N in wells ranged from 0.35 to 12.79 mg L^{-1}, while in the remainder of the wells, only two wells had elevated NO_3-N above 0.02 mg L^{-1}. The observed difference in groundwater nitrate concentrations between the Silver Springs springshed and the other springsheds is most likely a result of differences in nitrogen removal by denitrification due to differences in the confinement and depth to the Upper Floridan Aquifer. The Floridan Aquifer is largely unconfined, shallow, and oxic in the western half of the Silver Springs springshed, and the western springshed receives most of the nitrogen loading. The Wekiwa, Blue, Gemini, and DeLeon springsheds have a thicker confining layer, the Floridan Aquifer is generally deeper, and low dissolved oxygen is more prevalent (Boniol et al., 2014).

Reduced nitrogen forms were higher than NO_3-N in most of the surficial and intermediate aquifer wells as well as in Upper Floridan wells in confined (Wekiwa, Blue, Gemini, and De Leon) springsheds. In surficial and intermediate aquifer wells, concentrations of TKN were between 0 and 2.17 mg L^{-1}, with a median value of 0.22 mg L^{-1} (Table 3). Concentrations of NH_4-N were between 0 and 2.06 mg L^{-1}, with a median value of 0.14 mg L^{-1}. Upper Floridan wells in the Wekiwa, Blue, Gemini, and De Leon springsheds both had similar ranges (0–1.92 mg L^{-1}) and median values (0.19 mg L^{-1}) of TKN and NH_4-N, and ammonium made up 90% or more of the TKN in Upper Floridan wells with elevated reduced nitrogen concentrations (>0.2 mg L^{-1} TKN). The predominance of high ammonium concentrations in this region of the aquifer provides further evidence of the potential for DNRA to be an important mechanism for

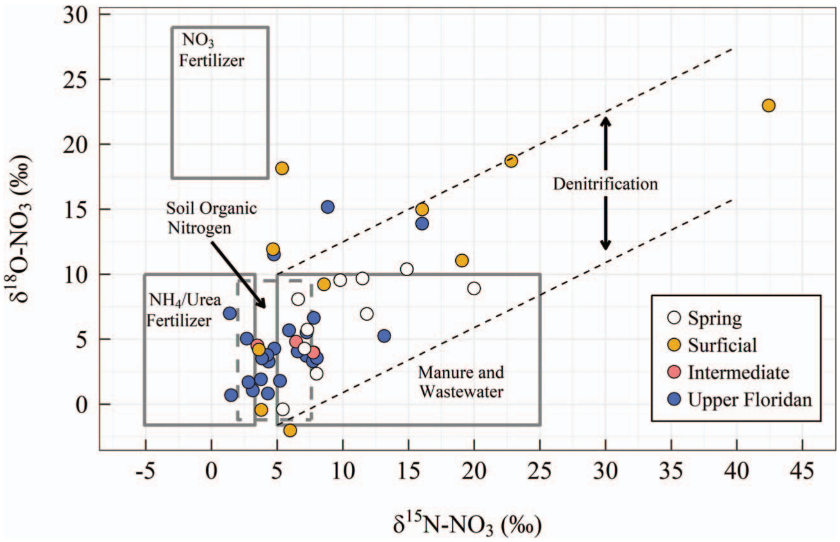

Figure 2. Biplot of nitrogen and oxygen stable isotopes for springs and wells. Source isotopic ranges are represented using boxes bounded by the emprical mean ± 2 standard deviations of the literature values used in the present study to model prior distributions. The approximate trajectory of denitrification (2:1, $\delta^{15}N$:$\delta^{18}O$) is overlaid for reference.

nitrate reduction that may compete with denitrification. Although DNRA is expected to be less favored than denitrification under the low organic carbon conditions found in the Floridan Aquifer, the presence of sulfide under reducing conditions in the aquifer may simultaneously inhibit denitrification and provide an electron donor for chemolithoautotrophic DNRA (Rye et al., 1981; Burgin and Hamilton, 2007).

Nitrate Isotope Measurements

Nitrate isotope values in springs samples were consistent with a denitrification influence for most springs (Table 2 and Figure 2). Four springs had isotope values that were not significantly elevated and had signatures that appeared consistent with either soil organic nitrogen (Alexander and Silver Glen Springs) or a mixture of fertilizer and wastewater/manure sources (Silver and Rock Springs). However, spring vent samples were not included in the Bayesian mixing model because of previously determined denitrification (Heffernan et al., 2012) and evidence that the spring vents are comprised of a mixture of old and new water (Toth and Katz, 2006). Dual isotope analysis of nitrate was performed in 38 of the 50 study wells, as 12 wells had nitrate concentrations that were below the quantitation limit for dual isotope analysis (Table 3). A majority of wells exhibited nitrate isotope signatures consistent with a mixture of fertilizer and wastewater/manure (Figure 2), and soil nitrogen was assumed to be a minor contributor to nitrate in wells because wells were selected for the study based on elevated nitrate concentrations from anthropogenic sources.

Heavy $\delta^{15}N$ and $\delta^{18}O$ values consistent with denitrification were observed in wells with low dissolved oxygen (<0.5 mg L^{-1}). Four surficial wells had low dissolved oxygen concentrations and isotope values that indicated that denitrification had occurred (Table 3). This was an unexpected result for a shallow, unconfined aquifer; generally, such aquifers are oxic, have high nitrate concentrations, and experience limited denitrification (Burow et al., 2010). Previous sampling of shallower (approximately 3 m) wells in the Wekiwa Springs area yielded higher nitrate concentrations than the present study (2.4 ± 0.3 mg L^{-1}), with less influence of denitrification (Tucker et al., 2014). The isotopic evidence for denitrification and the presence of reduced forms of nitrogen in surficial wells in the present study suggest that reducing conditions are more prevalent than previously known in the surficial aquifer and may allow for attenuation of nitrogen by denitrification in water prior to its recharging of the Floridan Aquifer.

Upper Floridan wells exhibited a spatial pattern in isotope values consistent with the forms of nitrogen. Wells in the mostly unconfined Silver Springs springshed showed no evidence for denitrification, consistent with the high dissolved oxygen concentrations and predominance of nitrate. Most Upper Floridan wells in the remaining springsheds had nitrate concentrations that were too low for dual isotope analysis. Based on the isotopic evidence for denitrification, wells with dissolved oxygen concentrations below 0.5 mg L^{-1} were excluded from mixing model analysis. These results highlight the need to verify the assumptions of limited influence of denitrification in isotopic nitrogen source studies as well as the value in adding additional tracers for nitrogen sources when reduced nitrogen species dominate in groundwater and preclude dual isotope analysis.

Wastewater Markers

Wastewater Markers in Springs

The wastewater markers sucralose, iohexol, and the chloride-to-bromide mass ratio (Cl:Br) were analyzed in springs and wells for confirmation of wastewater sources. Sucralose was detected at all springs except those with forested watersheds (Table 2), and concentrations were between 36 and 960 ng L^{-1}. The three springs with the highest sucralose concentrations (Sanlando, Starbuck, and Wekiwa) have high densities of septic tanks close to the springs but also have extensive application of reuse water in the area. Iohexol was analyzed in order to discriminate septic tank effluent from reuse water; however, it was not detected at any spring sites. Although iohexol has been used to detect runoff of reuse water irrigation in surface waters, there are still uncertainties in the photodegradation and soil biodegradation rates (Oppenheimer et al., 2018). Further confirmation that iohexol is an appropriate conservative tracer in groundwater may be necessary before its routine implementation as a reuse water tracer. The Cl:Br ratios were analyzed as an additional marker for wastewater contributions. Springs with Na-Cl water type had ratios reflective of a seawater Cl:Br ratio (Figure 3). This is consistent with previous work that identified relict seawater as the source of major ions in the middle reach of the St. Johns River (Belaineh et al., 2012). The remaining springs fell close to the mixing line between septic leachate and dilute groundwater.

An approximation of the contribution of wastewater (both septic effluent and reuse water) by volume to springs can be made based on dilution of sucralose assuming that (1) sucralose has approximately equal endmember concentrations in all wastewater sources and (2) soil adsorption and attenuation is negligible. Sucralose concentrations have been shown to be similar between septic tanks and reuse system effluent, with average concentrations between 40,000 and 50,000 ng L^{-1} (Oppenheimer et al., 2011; Schmidt et al., 2013; and SJRWMD, unpublished data). Using the range of observed sucralose concentrations at the spring sites, an approximate volumetric contribution of 0.1%–2.4% for wastewater sources is estimated for the study springs. Similar contributions by septic tank effluent (0.1%–1.0%) have been estimated using the artificial sweetener acesulfame in groundwater seeps in Ontario, Canada (Spoelstra et al., 2017). Under a hypothetical situation where only septic tank effluent or reuse water was the nitrogen source to a spring, an upper bound on the spring nitrate concentrations can be estimated. Based on literature values of total nitrogen concentrations in septic tank effluent (58 mg L^{-1}; Lusk et al., 2017) and reuse water (3–12 mg L^{-1}; Badruzzaman et al., 2012), nitrate concentrations of 1.4 and 0.29 mg L^{-1} are estimated as the upper bound for springs by septic effluent and reuse water, respectively. Actual contributions from each source are expected to be lower due to soil zone and aquifer attenuation processes. Attenuation of nitrogen from septic tank effluent and reuse water ranges from 40% to 75% and 50% to 85% in Florida soils, respectively (Eller and Katz, 2017, and references therein).

Wastewater Markers in Wells

In well samples, sucralose was widely distributed in unconfined aquifers, with detections in 50% and 65% of wells in the surficial aquifer and Upper Floridan wells within the Silver Springs springshed, respectively (Table 3). A statewide survey of sucralose in Florida water bodies (Silvanima et al., 2018) had a similar detection percentage for unconfined aquifers (30%, $n = 118$). Sucralose was detected in only three of 13 (23%) Upper Floridan wells in the springsheds with widespread confinement (Wekiwa, Blue, Gemini, and DeLeon). Iohexol was analyzed in five wells where reuse water was a potential source of nitrogen but was not detected (Table 3).

Concentrations of sucralose in unconfined wells were between 15 and 730 ng L^{-1}, except for one result of 16,000 ng L^{-1} (well L-1026). This high value of sucralose was measured in the surficial aquifer directly under a small wastewater treatment plant with direct land application of treated effluent and indicated that the well was directly in the plume of effluent. Two other wells (OR0894 and M-0771) also had notably high sucralose concentrations (580 and 730 ng L^{-1}) but likely differed in the source of nitrogen. At OR0894 (a surficial well), no reuse application was identified, but the surrounding number of septic tanks was 416. A paired Upper Floridan well at the same site also had detectable sucralose (220 ng L^{-1}), indicating a local region of poor confinement. At M-0771, there were 428 septic tanks in the surrounding area, but a golf course utilizing reuse water for irrigation was immediately adjacent and upgradient of the well. Additionally, most of the septic tanks at this site were downgradient on the potentiometric surface. Overall, sucralose concentrations in wells were lower than the respective springs, which suggests there may be a disproportionate

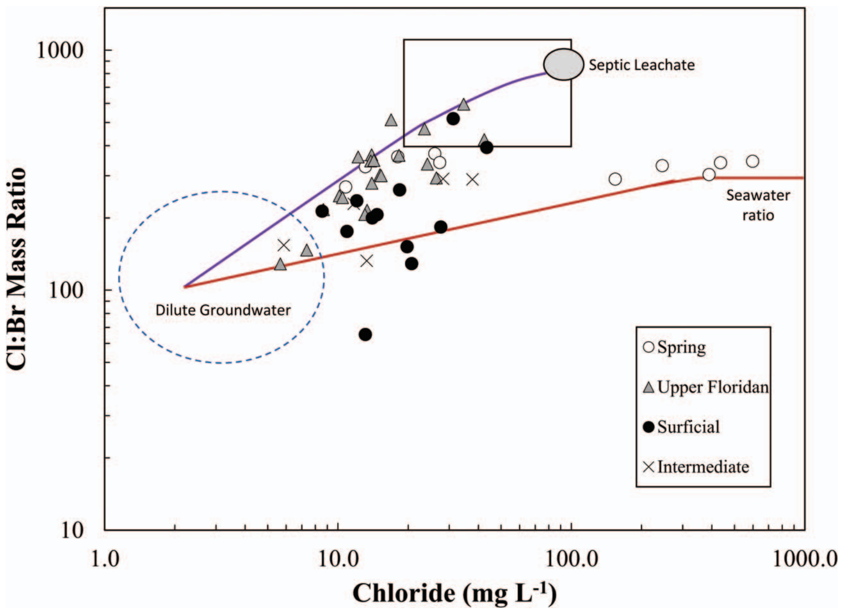

Figure 3. Mass ratio of chloride to bromide versus chloride concentration in springs and study wells. Dilute groundwater endmember is from Davis et al. (2004), and septic leachate endmember is from Panno et al. (2006). The target area for septic leachate influence is represented by the black box (Katz et al., 2011). Binary mixing lines between septic leachate and dilute groundwater and between seawater and dilute groundwater are shown in purple and red, respectively.

contribution from wastewater nitrogen sources near the springs that was not adequately sampled rather than elevated nitrogen from wastewater sources throughout the springsheds.

Surficial and intermediate aquifer well Cl:Br mass ratios fell between the seawater-dilute groundwater and septic leachate-dilute groundwater mixing lines. Based on a previous comparison of nitrogen isotope data and Cl:Br mass ratios in groundwater and springs (FDEP, unpublished data), sites with an inorganic nitrogen source generally had Cl:Br ratios below 400. Nitrogen isotope data that were consistent with an organic nitrogen source typically corresponded to more variable Cl:Br ratios but were generally greater than 400. Four Upper Floridan Aquifer wells had high Cl:Br ratios (>400). All four wells were in areas with high densities of septic tanks and, in the case of two wells (M-0771 and M-0786), extensive application of reuse water. Two surficial wells (S-0716 and V-0814) had Cl:Br ratios >400; however, sucralose was not detected in either well. Other wells where sucralose was detected (up to 16,000 ng L^{-1}) all had Cl:Br ratios less than 300, which may have resulted due to dilution of conservative ions by rainwater.

Bayesian Mass Balance Mixing Model Predictions of Nitrate-Nitrogen Sources

A Bayesian mass-balance–based mixing model was developed using dual nitrate isotope data from wells to estimate the fractional contribution of four nitrogen sources: wastewater, ammonium fertilizer and synthetic organic N fertilizers, nitrate fertilizer, and manure. The use of informative Dirichlet priors derived from land use is in contrast to previous mixing model studies of nitrate sources that implemented either vague (equal contributions of sources) Dirichlet priors (Xue et al., 2012; Yang et al., 2013; and Yang and Toor, 2016) or an informative prior for a single nitrogen source (soil organic nitrogen) across all sites (Ransom et al., 2016). Unequal prior means here were justified by relatively homogeneous distributions of land uses around well sites as well as similar agricultural use (pasture and field crops) at most agricultural sites. The present use of informative priors is analogous to isotope-based Bayesian mixing models of animal diets, where informative priors were assigned based on gut content analysis (Moore and Semmens, 2008). An advantage of using informative priors is that nitrogen sources with overlapping distributions of isotope values may be better discriminated based on prior knowledge of their contributions from an independent source of information.

Wastewater Sources

Posterior geometric means for the fractional contribution of wastewater sources (defined as both septic effluent and land-applied reuse water) were between <0.01 and 0.27 for agricultural areas and between

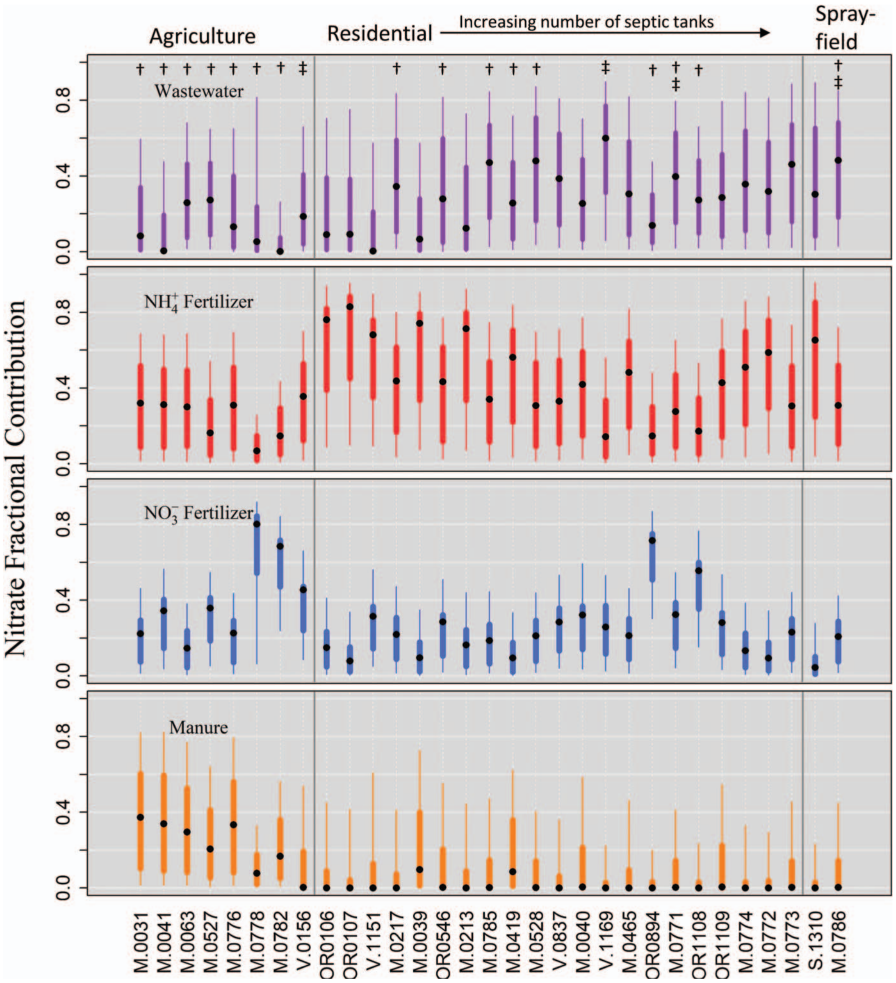

Figure 4. Mixing model predicted fractional source contributions of groundwater nitrate in study wells. The geometric mean (black dot), 68% credible interval (thick line), and 95% credible interval (thin line) are shown for each well. Detection of sucralose (†) and Cl:Br ratios >400 (‡) are indicated on the wastewater panel. Wastewater refers to both septic tank effluent and land-applied treated wastewater.

<0.01 and 0.60 for residential areas (Figure 4). Evaluation of the central tendencies of the model results across wells allows for generalization, but the utility of Bayesian mixing models over traditional mixing models is the ability to characterize uncertainty around estimates of source contribution. For wastewater, the 95% credible intervals were large for most wells and were likely a result of the overlap in source isotopic distributions.

Contributions of wastewater in agricultural areas were further confirmed by wastewater markers at all sites that were classified primarily as agricultural. These sites were primarily in the Silver Springs springshed and had septic tanks (44–152) in the 1-km buffer area, and sucralose concentrations were relatively low (15–41 ng L^{-1}). For wells in residential areas, the mean fractional contribution of wastewater showed a weakly increasing trend with higher densities of septic tanks, and there was good agreement between wastewater indicators and elevated contributions of wastewater sources (sucralose concentrations between 15 and 730 ng L^{-1}). Wells directly below areas with land-applied treated wastewater had contrasting results: well S-1310 had a mean wastewater contribution close to the prior mean (0.30), and no wastewater markers were detected, whereas well M-0786 had higher predicted mean contribution from wastewater (0.48), and both sucralose and Cl:Br ratios indicated wastewater influence. These differences may be due to differences in nitrogen attenuation between sites but also may be due to well locations, as the monitoring wells were not sited with the specific intent of monitoring treated wastewater application.

Fertilizer Sources

In agricultural areas, central tendencies were between 0.07 and 0.36 for ammonium fertilizer and

Table 3. *Water quality parameters and source indicators in study wells (* = not detected, ** = not analyzed). Water Reuse abbreviations are: RIB: Rapid Infiltration Basin (land application at wastewater treatment facilities); Perc: Percolation Pond (Land application of treated wastewater from small treatment facilities); RI: Residential Irrigation; GCI: Golf Course Irrigation; SF: Sports Facilities.*

Well Site	Well ID	Aquifer	Springshed	Well Depth (ft)	Primary N-Contributing Land Use	Septic Tanks (1-km radius)	Water Reuse (1-km radius)	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	TKN (mg L^{-1})	$\delta^{15}N$-$NO_{3\ Air}$ (‰)	$\delta^{18}O$-$NO_{3\ VSMOW}$ (‰)[1]	DO (mg L^{-1})	Sucralose (ng L^{-1})	Cl:Br
1	OR0107	SA	Wekiwa	40	Residential	29	RI	0.16	0.01	0.18	3.79	– 0.44	7.5	*	207
2	S-1015	SA	Wekiwa	50	Residential	297	—	0.03	0.36	1.52	5.37	18.15	0.2	48	152
3	L-1026	SA	Wekiwa	47	Residential	338	RIB, Perc	*	2.06	2.17	**	**	0.2	16,000	184
4	OR0894	SA	Wekiwa	20	Residential	416	—	0.04	0.35	1.39	4.69	11.92	0.9	580	176
5	OR0661	SA	Wekiwa	44	Residential	596	—	0.11	0.66	0.86	42.42	22.98	0.2	46	129
6	OR1108	SA	Wekiwa	39	Residential	618	RI	1.32	0.01	0.04	8.57	9.22	2.8	38	236
7	V-0197	SA	Blue	30	Residential	18	RI	0.71	*	0.08	22.82	18.71	0.3	240	262
8	V-1151	SA	Blue	37	Residential	56	—	0.59	0.03	0.15	3.61	4.20	4.9	*	65
9	V-0814	SA	Blue	42	Residential	302	Perc, RI	0.25	0.19	0.22	19.07	11.06	0.4	*	394
10	S-0716	SA	Gemini	20	Residential	196	SF	0.02	0.39	1.25	**	**	0.2	*	519
11	S-1310	SA	Gemini	35	Land-applied wastewater	0	RIB	0.05	0.06	0.15	5.99	– 2.02	1.7	*	200
12	V-1028	SA	DeLeon	50	Dairy and field crops	27	—	0.06	0.14	0.34	16.04	14.98	0.2	*	214
13	OR0651	IA	Wekiwa	72	Forested	0	—	*	0.2	0.22	**	**	0.2	*	290
14	OR0546	IA	Wekiwa	60	Residential	82	—	0.72	0.04	0.26	7.75	3.97	5.7	44	291
6	OR1109	IA	Wekiwa	90	Residential	618	RI	0.04	0.12	0.15	3.49	4.52	0.9	*	154
15	V-0837	IA	Blue	60	Residential	334	GCI	0.13	*	*	6.44	4.82	6.3	*	229
10	S-0717	IA	Gemini	64	Residential	196	SF	0.04	1.14	1.57	**	**	0.2	*	133
16	M-0776	UFA	Silver	50	Pasture and field crops	44	—	12.79	*	0.05	6.56	4.06	5.6	15	*
17	M-0782	UFA	Silver	195	Pasture and field crops	52	—	10.10	*	*	4.75	11.51	7.2	26	303
18	M-0778	UFA	Silver	55	Pasture and field crops	76	—	0.86	0.01	0.06	16.03	13.89	0.6	16	247
19	M-0041	UFA	Silver	80	Pasture and field crops	81	—	1.60	0.02	0.06	5.90	5.69	4.3	15	*
20	M-0031	UFA	Silver	66	Pasture and field crops	96	—	1.86	*	*	4.79	4.27	5.7	34	*
21	M-0527	UFA	Silver	120	Pasture and field crops	111	—	2.49	*	*	7.79	6.64	4.3	41	367
22	M-0063	UFA	Silver	120	Pasture and field crops	144	—	1.62	0.02	*	4.35	3.27	5.6	19	*
23	M-0217	UFA	Silver	60	Residential	65	SF	1.88	0.01	0.08	4.26	3.78	3.5	26	147
24	M-0039	UFA	Silver	40	Residential	81	—	2.64	*	0.09	1.50	0.70	5.1	*	*
25	M-0213	UFA	Silver	30	Residential	108	—	0.39	*	0.09	3.77	1.91	3.4	*	*
26	M-0785	UFA	Silver	90	Residential	135	—	0.65	*	0.08	7.71	3.30	4.7	41	243
27	M-0419	UFA	Silver	64	Residential	138	—	0.95	*	*	3.15	1.05	6.3	15	129
28	M-0040[2]	UFA	Silver	90	Residential	347	GCI	0.35	*	*	2.68	5.04	2.9	*	*
29	M-0465	UFA	Silver	120	Residential	413	—	0.73	*	*	3.85	3.52	5.5	*	*
30	M-0771[2]	UFA	Silver	72	Residential	428	GCI	7.99	*	0.06	7.24	5.53	1.7	730	596
31	M-0774	UFA	Silver	90	Residential	658	—	3.35	*	0.05	5.21	1.79	5.5	*	335

Table 3. *Continued.*

Well Site	Well ID	Aquifer	Springshed	Well Depth (ft)	Primary N-Contributing Land Use	Septic Tanks (1-km radius)	Water Reuse (1-km radius)	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	TKN (mg L^{-1})	δ^{15}N-$NO_{3\ Air}$ (‰)	δ^{18}O-$NO_{3\ VSMOW}$ (‰)[1]	DO (mg L^{-1})	Sucralose (ng L^{-1})	Cl:Br
32	M-0772	UFA	Silver	49	Residential	865	GCI	0.40	*	*	4.29	0.83	5.8	*	*
33	M-0773[2]	UFA	Silver	47	Residential	1085	—	1.88	*	*	7.78	3.99	3.4	*	359
34	M-0528[2]	UFA	Silver	135	Residential	183	SF	2.18	*	*	7.22	3.73	3.2	98	345
35	M-0786[2]	UFA	Silver	52	Land-applied wastewater	106	Sprayfield	2.58	*	*	8.02	3.55	3.9	180	512
1	OR0106	UFA	Wekiwa	395	Residential	29	RI	0.02	0.05	0.12	2.81	1.70	0.8	*	*
14	OR0548	UFA	Wekiwa	155	Residential	82	—	0.01	0.02	0.09	**	**	0.1	190	300
2	S-1014	UFA	Wekiwa	300	Residential	297	—	0.01	1.31	1.44	**	**	0.1	*	207
4	OR0893	UFA	Wekiwa	140	Residential	416	—	0.01	1.72	1.92	46.37	26.83	0.1	220	215
6	OR1110	UFA	Wekiwa	180	Residential	618	RI	0.02	0.18	0.19	8.85	15.18	0.1	*	*
7	V-0196	UFA	Blue	234	Residential	18	RI	*	0.04	0.07	**	**	0.2	*	217
8	V-1152	UFA	Blue	140	Residential	56	—	*	0.01	*	**	**	0.2	*	279
9	V-0810	UFA	Blue	311	Residential	302	Perc, RI	0.02	1.19	1.27	**	**	0.6	*	309
36	V-1169	UFA	Blue	137	Residential	365	RIB, RI	1.30	*	*	13.15	5.25	6.6	*	470
11	S-1230	UFA	Gemini	404	Land-applied wastewater	0	RIB	*	0.47	0.53	**	**	0.2	*	293
37	S-1408	UFA	Gemini	200	Land-applied wastewater	94	RIB, RI	*	0.83	0.90	**	**	0.1	120	347
12	V-1030	UFA	DeLeon	200	Dairy and field crops	27	—	*	0.42	0.60	**	**	0.1	*	365
38	V-0156	UFA	DeLeon	195	Plant nursery	152	Perc	9.87	*	*	1.40	6.99	4.4	*	424

[1]VSMOW = Vienna Standard Mean Ocean Water.
[2]Iohexol analyzed but not detected.

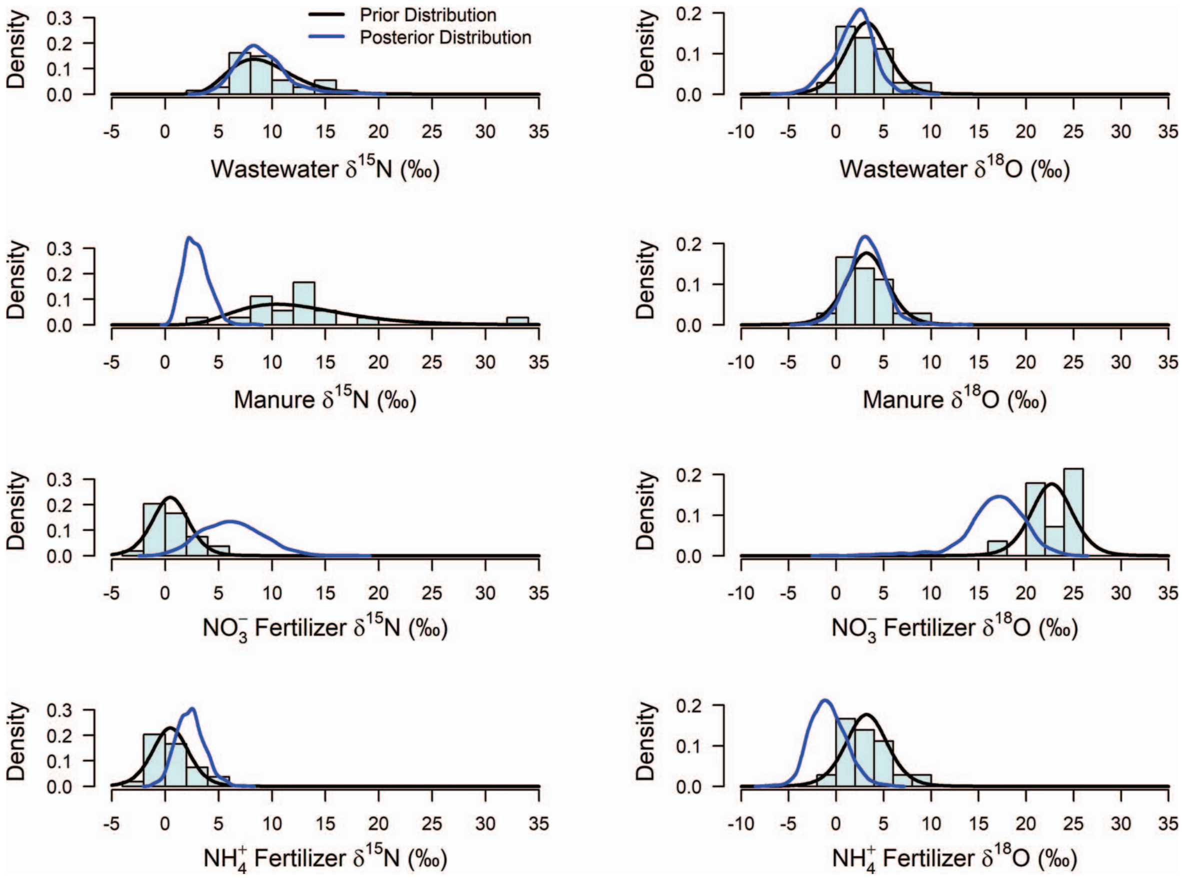

Figure 5. Source nitrate isotope empirical distributions (blue bars), prior probability density (black lines), and posterior probability densities predicted by the mixing model (blue lines).

between 0.15 and 0.80 for nitrate fertilizer (Figure 4). Taken together, the two types of fertilizer had modeled mean contributions of 50%–80% in agricultural areas. High contributions from synthetic fertilizer are consistent with previous work in Florida springs within agricultural springsheds that demonstrated that synthetic fertilizer was a dominant nitrogen source over organic nitrogen sources (i.e., wastewater and manure) (Katz, 2004; Heffernan et al., 2012). In some cases, high contributions of nitrate fertilizer may have been a result of legacy agricultural impacts. For example, regionally high nitrate from defunct citrus operations are known to be present in the groundwater near well M-0782 as well as in converted citrus groves in the greater Orlando area, where Wekiwa, Rock, Sanlando, and Starbuck springs are found (Canion, 2017).

In residential wells, central tendencies were between 0.14 and 0.83 for ammonium fertilizer and between 0.08 and 0.71 for nitrate fertilizer (Figure 4). The combined mean contributions of fertilizer sources were modeled between 40% and 100%, with landscape fertilization as the most likely source. The 95% credible intervals were large for ammonium fertilizer but were smaller for nitrate fertilizer, which could be attributed to the unique range of nitrate fertilizer $\delta^{18}O$ values. Contributions from ammonium fertilizer were markedly lower at sites where elevated contributions from wastewater were predicted. Contributions from nitrate fertilizer were generally close to prior distributions, indicating that there was little evidence in the data to shift the prior distribution. Wells OR894 and OR1108 were notable exceptions and had posterior mean contributions of 0.71 and 0.56 for nitrate fertilizer, respectively. Well OR894 illustrates a potential pitfall in relying on nitrate isotope data for source attribution when reduced forms of nitrogen have higher concentrations. Nitrogen in this well was mostly in the form of TKN (1.39 mg L^{-1}), and the sucralose concentration was relatively high (580 ng L^{-1}), which indicated that the wastewater contribution was higher than predicted by the mixing model.

Manure Sources

Modeled mean manure source contributions were between <0.01 and 0.37 at agricultural sites and between <0.01 and 0.10 at residential sites (Figure 4). Manure posterior means at agricultural sites were similar to prior means, indicating that there was insufficient evidence in the data to shift the informative prior distributions of the manure sources. Low contributions from manure may be attributed to the predominance of pasture for beef cattle and horses. Pasture operations in Florida have been shown to have limited nitrogen loading to groundwater when managed properly (Sigua, 2010). Concentrated manure sources, including dairies and horse manure stockpiles, may still contribute nitrogen locally but were not targeted for sampling in the present study. One well cluster was adjacent to a dairy (V-1028 and V-1030); however, low dissolved oxygen prevented the use of nitrate isotope data from these wells. For areas with agricultural influence, better constraints on the relative contribution of manure and wastewater may be improved by the addition of boron isotope measurements, which have greater distinction between the two sources (Komor, 1997; Vengosh, 1998).

Posterior Distributions of Source Isotope Values

In addition to probabilistic estimates of fractional source contributions, the Bayesian mixing model produces posterior distributions for the source isotope values that can be used to evaluate model results (Figure 5). For wastewater sources, both $\delta^{15}N$ and $\delta^{18}O$ had posterior distributions that closely followed prior distributions. Manure sources showed a clear shift to a lower mean (2.9‰) and variance for $\delta^{15}N$ in the posterior distribution. These lower values are not consistent with literature data and indicate that the model may be overpredicting manure contributions.

Both NO_3^- and NH_4^+ fertilizers exhibited some degree of alteration in posterior distributions of $\delta^{15}N$ and $\delta^{18}O$. For NO_3^- fertilizer, the prior mean for $\delta^{15}N$ was shifted from 0.49‰ to 6.3‰ in the posterior distribution, and the mean for $\delta^{18}O$ was shifted from 22.7‰ to 16.8‰. This shift was likely caused by the influence of denitrification, as groundwater that has experienced partial denitrification may have $\delta^{15}N$ values between the fertilizer and wastewater ranges and $\delta^{18}O$ values slightly below the NO_3^- fertilizer range. Smaller shifts in posterior distribution were observed for NH_4^+ fertilizer. Mean $\delta^{15}N$ and $\delta^{18}O$ were shifted from 0.49‰ to 2.3‰ and 3.2‰ to −0.86‰, respectively.

SUMMARY AND CONCLUSIONS

In the present study, we used multiple lines of evidence, including dual nitrate isotope analysis and wastewater markers, to attribute sources of elevated groundwater nitrate in wells and springs. The influence of denitrification precluded the modeling of nitrate sources at spring vents; however, sucralose concentrations indicated that wastewater contributed to all springs with developed springsheds. For wells, Bayesian mixing models indicated that, in general, fertilizer sources were the largest contributor to groundwater nitrate or had approximately equal contributions with wastewater and manure sources. Legacy fertilizer from past citrus production contributes an as-yet-undetermined amount of this fertilizer nitrogen in some regions of the study area. Detections of sucralose at agricultural sites and a shifted posterior $\delta^{15}N$ distribution for manure sources suggests that manure sources may contribute less than predicted by the model in agricultural areas. The addition of manure specific tracers in future studies (e.g., boron isotopes) may provide better predictions of manure contributions. At residential sites, agreement between predicted wastewater contributions, high total nitrogen concentrations, and sucralose detections provided evidence for localized impacts from wastewater sources. In the areas where many of the residential wells were sited, low concentrations of nitrate and the presence of reduced nitrogen (NH_4-N and TKN) precluded dual nitrate isotope analysis, which illustrates the utility of additional wastewater tracers. Septic effluent and reuse water were lumped into a single wastewater category for the mixing model, but based on higher total nitrogen concentrations in septic tank effluent than reuse water, it is expected that septic tanks contribute more to nitrogen in groundwater. Exceptions may occur where overapplication of reuse water occurs in geologically sensitive areas. Further development of reuse-specific tracers would help determine whether reuse water contributes any appreciable nitrogen to groundwater.

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Table A1. *Land use percentages and Dirichlet prior parameters for wells.*

	2014 Land Use Fraction									Dirichlet Parameter (alpha)			
Site	Urban/ Built-Up	Agriculture	Upland	Forest	Water	Wetland	Transportation/ Barren	Septic Tanks within 1-km Radius	Water Reuse within 1-km Radius	Wastewater	Nitrate Fertilizer	Ammonia Fertilizer	Manure
L-1026	0.42	0.03	0.03	0.05	0.31	0.12	0.03	338	Percolation pond; RIB	—	—	—	—
M-0031	0.23	0.68	0.03	0.05	0.00	0.00	0.00	96	—	0.5	1	1	1
M-0039	0.39	0.10	0.11	0.31	0.00	0.01	0.07	81	—	0.5	1	1	0.5
M-0040	0.81	0.01	0.02	0.07	0.01	0.03	0.06	347	Golf course	1	1	1	0.2
M-0041	0.07	0.56	0.03	0.33	0.00	0.00	0.00	81	—	0.2	1	1	1
M-0063	0.35	0.53	0.01	0.12	0.00	0.00	0.00	144	—	1	1	1	1
M-0213	0.85	0.00	0.04	0.07	0.00	0.01	0.02	108	—	0.5	1	1	0.1
M-0217	0.87	0.00	0.02	0.07	0.01	0.00	0.02	65	Recreational facilities	1	1	1	0.1
M-0419	0.34	0.19	0.39	0.05	0.00	0.00	0.03	138	—	1	1	1	0.5
M-0465	0.79	0.01	0.02	0.11	0.00	0.01	0.05	413	—	1	1	1	0.1
M-0527	0.21	0.50	0.07	0.20	0.00	0.00	0.03	111	—	1	1	1	1
M-0528	0.42	0.09	0.02	0.38	0.00	0.01	0.08	183	—	1	1	1	0.2
M-0771	0.57	0.19	0.22	0.02	0.00	0.00	0.00	428	Golf course	1	1	1	0.2
M-0772	0.72	0.00	0.02	0.11	0.06	0.08	0.02	865	Golf course	1	1	1	0.1
M-0773	0.83	0.02	0.04	0.08	0.00	0.01	0.03	1085		1	1	1	0.2
M-0774	0.79	0.00	0.00	0.19	0.00	0.01	0.01	658	—	1	1	1	0.1
M-0776	0.20	0.45	0.04	0.24	0.05	0.00	0.02	44	—	0.5	1	1	1
M-0778	0.22	0.74	0.01	0.02	0.00	0.00	0.01	76	—	0.5	1	1	1
M-0782	0.10	0.56	0.00	0.32	0.00	0.02	0.00	52	—	0.2	1	1	1
M-0785	0.23	0.38	0.02	0.31	0.01	0.01	0.05	135	—	1	1	1	0.2
M-0786	0.21	0.71	0.00	0.03	0.00	0.00	0.06	106	Large wastewater sprayfield	1	1	1	0.2
OR0106	0.25	0.11	0.07	0.29	0.00	0.09	0.20	29	Residential irrigation	0.5	1	1	0.1
OR0107	0.25	0.11	0.07	0.29	0.00	0.09	0.20	29	Residential irrigation	0.5	1	1	0.1
OR0546	0.48	0.00	0.01	0.11	0.01	0.39	0.00	82	—	0.5	1	1	0.2
OR0548	0.48	0.00	0.01	0.11	0.01	0.39	0.00	82	—	—	—	—	—
OR0651	0.01	0.00	0.14	0.50	0.00	0.35	0.00	0	—	—	—	—	—
OR0661	0.88	0.01	0.03	0.05	0.00	0.00	0.03	596	—	—	—	—	—
OR0893	0.55	0.00	0.00	0.27	0.00	0.17	0.00	416	—	—	—	—	—

Table A1. *Continued.*

	2014 Land Use Fraction									Dirichlet Parameter (alpha)			
Site	Urban/ Built-Up	Agriculture	Upland	Forest	Water	Wetland	Transportation/ Barren	Septic Tanks within 1-km Radius	Water Reuse within 1-km Radius	Wastewater	Nitrate Fertilizer	Ammonia Fertilizer	Manure
OR0894	0.55	0.00	0.00	0.27	0.00	0.17	0.00	416	—	1	1	1	0.1
OR1108	0.78	0.02	0.03	0.04	0.02	0.08	0.03	618	Residential irrigation	1	1	1	0.1
OR1109	0.78	0.02	0.03	0.04	0.02	0.08	0.03	618	Residential irrigation	1	1	1	0.2
OR1110	0.78	0.02	0.03	0.04	0.02	0.08	0.03	618	Residential irrigation	—	—	—	—
S-0716	0.39	0.07	0.00	0.12	0.22	0.20	0.00	196	Recreational facilities	—	—	—	—
S-0717	0.39	0.07	0.00	0.12	0.22	0.20	0.00	196	Recreational facilities	—	—	—	—
S-1014	0.76	0.00	0.02	0.03	0.02	0.13	0.04	297	—	—	—	—	—
S-1015	0.76	0.00	0.02	0.03	0.02	0.13	0.04	297	—	—	—	—	—
S-1230	0.00	0.09	0.21	0.46	0.02	0.12	0.10	0	RIB	—	—	—	—
S-1310	0.00	0.09	0.21	0.46	0.02	0.12	0.10	0	RIB	1	1	1	0.1
S-1408	0.74	0.00	0.02	0.01	0.02	0.07	0.13	94	Multiple ribs and irrigation	—	—	—	—
V-0156	0.23	0.27	0.06	0.40	0.00	0.05	0.00	152	Percolation pond	1	1	1	0.2
V-0196	0.66	0.01	0.02	0.14	0.06	0.05	0.07	18	Residential irrigation	—	—	—	—
V-0197	0.66	0.01	0.02	0.14	0.06	0.05	0.07	18	Residential irrigation	—	—	—	—
V-0810	0.43	0.03	0.00	0.29	0.13	0.13	0.00	302	Percolation pond; residential Irrigation	—	—	—	—
V-0814	0.43	0.03	0.00	0.29	0.13	0.13	0.00	302	Percolation pond; residential irrigation	—	—	—	—
V-0837	0.42	0.00	0.41	0.11	0.00	0.02	0.04	334	Golf course	1	1	1	0.1
V-1028	0.05	0.27	0.06	0.35	0.06	0.21	0.00	27	—	—	—	—	—
V-1030	0.05	0.27	0.06	0.35	0.06	0.21	0.00	27	—	—	—	—	—
V-1151	0.06	0.00	0.14	0.64	0.00	0.16	0.00	56	—	0.2	1	1	0.1
V-1152	0.06	0.00	0.14	0.64	0.00	0.16	0.00	56	—	—	—	—	—
V-1169	0.41	0.07	0.16	0.33	0.00	0.00	0.03	365	RIB; residential irrigation	1	1	1	0.1

Table A2. *List of references used to model source prior distributions.*

Tracer	Nitrogen Source	n	References
δ15N	Wastewater	38	Widory et al., 2004; Accoe et al., 2008; Hinkle et al., 2008; Panno et al., 2008; Katz et al., 2010 Briand et al., 2017
	NH_4 fertilizer	14	Vitòria et al., 2004; Widory et al., 2004; Bateman & Kelly, 2007; Briand et al., 2017
	NO_3 fertilizer	282	Vitòria et al., 2004; Accoe et al., 2008; Davis et al., 2015; Michalski et al., 2015
	Manure	18	Widory et al., 2004; Bateman and Kelly, 2007; Accoe et al., 2008; Panno et al., 2008; Briand, 2017
δ18O	Wastewater	23	Accoe et al., 2008; Panno et al., 2008; Katz et al., 2010; Briand et al., 2017
	NH_4 fertilizer	23	Accoe et al., 2008; Panno et al., 2008; Katz et al., 2010; Briand et al., 2017
	NO_3 fertilizer	292	Vitòria et al., 2004; Accoe et al., 2008; Davis et al., 2015; Michalski et al., 2015
	Manure	23	Accoe et al., 2008; Panno et al., 2008; Briand et al., 2017; Katz et al., 2010

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