Technical Report: Little Lagoon Watershed Nutrient Assessment and Source Tracking

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Technical Summary

Little Lagoon is a groundwater-dominated, coastal estuary with a documented history of harmful algal blooms and other water quality concerns. The timing and magnitude of harmful algal blooms has been correlated to periods of elevated groundwater discharge, suggesting that groundwater-derived nutrients are in part responsible for algal growth (i.e., eutrophication). Potential sources of groundwater nutrients within the Little Lagoon watershed include land application of fertilizers, onsite wastewater treatment system effluent, centralized wastewater treatment effluent disposal to groundwater, and natural decomposition and remineralization of soil organic material.

In order to determine whether anthropogenic activities within the Little Lagoon watershed are contributing nutrients to groundwater (and therefore to the Lagoon), a comprehensive groundwater quality assessment was completed for the surficial aquifer that discharges to Little Lagoon. Groundwater samples were collected throughout the watershed across a gradient of land uses from existing monitoring wells, newly-installed monitoring wells, irrigation wells, temporary piezometers, groundwater seeps, and groundwater-fed canals. Samples were analyzed for nutrients (i.e., ammonia, nitrate, nitrite, total dissolved nitrogen, dissolved organic nitrogen, reactive phosphorous, and total dissolved phosphorous) and related explanatory parameters. Spatial anomalies of elevated nutrients (i.e., hotspots) were compared with proximal land use activities to screen for potential sources. Secondary analyses of stable nitrogen and oxygen isotopes as well as terrain and drainage modeling were used to further discriminate probably sources of nutrients. Lastly, geochemical and hydraulic conditions within the aquifer and subterranean estuary were evaluated to predict subsurface fate and transport of nutrients.

Two spatial anomalies containing elevated nutrient concentrations were revealed from the groundwater sampling: one on the southeastern shore of the Lagoon in an area of commercial and residential development and another on the northern, central shore around the Brigadoon subdivision downgradient of the Baldwin County Sewer Services (BCSS) wastewater treatment plant. The anomaly on the southeastern shore contained elevated total dissolved nitrogen, dissolved organic nitrogen, and ammonia. Stable nitrogen isotope analyses of persulfate digested subsamples (i.e., total dissolved nitrogen) suggests a natural source – most likely remineralized and partially decayed soil organic material. This finding is consistent with studies conducted in other nearby estuaries.

The second anomaly around the Brigadoon subdivision and BCSS wastewater treatment plant contained elevated total dissolved nitrogen, dissolved organic nitrogen, ammonia, nitrate, reactive phosphorous, and total dissolved phosphorous. Stable nitrogen and oxygen isotope analyses of nitrate subsamples suggest a mixture of fertilizer and natural sources of nitrate. Stable nitrogen isotope analyses of digested subsamples suggest that the reduced forms of nitrogen (i.e., ammonia and dissolved organic nitrogen) are from a natural source – consistent with the reduced dissolved nitrogen anomaly on the southeastern shore. There is no compelling evidence to suggest a wastewater source (onsite or centralized) of dissolved nitrogen to groundwater in the areas that were sampled.

The source of reactive phosphorous and total dissolved phosphorous in the anomaly around the Brigadoon subdivision and BCSS wastewater treatment plant is more difficult to discern as there is no reliable stable isotope analysis available to discriminate phosphorous sources. However, spatial as well as terrain and drainage modeling evidence suggests that the effluent percolations ponds used by the BCSS wastewater treatment plant for effluent disposal are the most likely source of the dissolved phosphorous anomaly.

Geochemical conditions within the surficial aquifer surrounding Little Lagoon and within the subterranean estuary are generally favorable for nitrate reduction and transformation via denitrification. However, these same conditions are less favorable for nitrogen oxidation, aerobic biodegradation, and phosphorous adsorption. Therefore, application of reduced forms of nitrogen (i.e., ammonia and dissolved organic nitrogen) and phosphorous to land surfaces within the Little Lagoon watershed warrants concern due to an increased risk of eutrophication. Additional monitoring of phosphorous in the vicinity of the wastewater treatment plant, and contingent on monitoring results, possible changes in wastewater treatment and disposal practices, are likely needed to protect and preserve the quality of water and ecology in Little Lagoon.

Plain Language Summary

Little Lagoon has a documented history of toxin-releasing, harmful algal blooms. These harmful algal blooms are likely fueled by nutrients in the form of nitrogen and phosphate that are washed from the land into the Lagoon by rain and groundwater flow. There are multiple sources of nutrients to the environment including fertilizer application, wastewater disposal, and natural biological processes in the soil.

The purpose of this study was to determine the source of nutrients to Little Lagoon. Groundwater samples were collected from wells and springs around the Lagoon and analyzed for nutrients. Groundwater samples with elevated nutrient concentrations were compared to nearby land uses to screen for possible sources. Additional forensic analyses were used to further discriminate sources.

The majority of nitrogen nutrients in groundwater surrounding the Lagoon is attributed to natural soil processes – notably the natural decay of plant material deposited by the numerous marshes and forests throughout the watershed. Fertilizer is only a minor, localized contributor of nitrogen. Phosphorous nutrients are most likely caused by wastewater effluent disposal at the Baldwin County Sewer Services (BCSS) centralized wastewater treatment plant; however, the data generated from this project are not sufficient to confirm these findings. Additional monitoring of phosphorous in the vicinity of the wastewater treatment plant, and contingent on monitoring results, possible changes in wastewater treatment and disposal practices, are warranted to protect and preserve the quality of water and ecology in Little Lagoon.

Rationale

Little Lagoon is a shallow (~1.5-m average depth) coastal lagoon with a surface area of 1,052 hectares, located about 20 km to the east of the mouth of Mobile Bay in the northern Gulf of Mexico (Figure 1). The shallow hydrogeology of Little Lagoon is characterized by a sandy surficial aquifer with a thickness of approximately 30 m and annual precipitation exceeding 165 cm (Chandler et al., 1985; Robinson et al., 1996). Rapid infiltration through the sandy soils precludes surface runoff, and no major defined surficial drainage network exists in the lagoon's watershed (Waselkov et al., 2022). Little Lagoon receives groundwater and exchanges surface water with the Gulf of Mexico through a stabilized inlet (Liefer et al., 2009; Su et al., 2014). The restricted inlet dampens diurnal tidal exchange, and like much of the northern Gulf of Mexico, the tidal range in the lagoon is low (<0.3 m; Liefer et al., 2014).

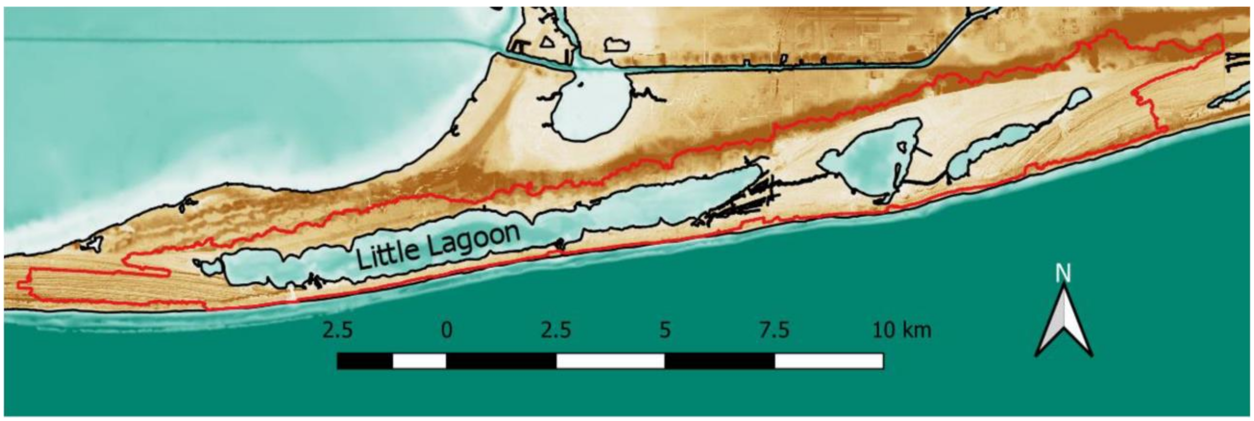

Figure 1 – Digital elevation model of region surrounding Little Lagoon. Topographically delineated watershed boundary shown in red. Groundwater flow likely crosses watershed boundary in areas due to groundwater pumping and injection.

A well-documented relationship exists in Little Lagoon between seasonal groundwater related nutrient loading and harmful algal blooms (HABs) of *Pseudo-nitzschia* spp., which tend to peak in abundance during early spring (Liefer et al., 2009; Liefer et al., 2013; Bernard et al., 2014; Liefer et al., 2014; Bernard et al., 2015), possibly in response to the timing of late winter storms and warming surface water temperatures (Beebe et al., 2022). Su et al. (2012 and 2014) used radon and radium radioisotopes to investigate the temporal relationships between groundwater discharge and surface water nutrients and chlorophyll-a and determined that elevated groundwater discharge was a significant driver for HABs. Su et al. (2012 and 2014) also determined rates of groundwater discharge from radon and radium inventories. However, Su et al. (2012 and 2014) did not distinguish between fresh and saline groundwater discharge or investigate the sources of nutrients.

Determining the source of nutrients to Little Lagoon is an important step in managing and addressing threats to the health and resilience of this unique estuary. Previous and ongoing research overseen by the principal investigator (PI) has revealed extensive plumes of nitrogen-enriched groundwater entering Little Lagoon along the shoreline (Figure 2). These submarine groundwater plumes have distinct geochemical properties compared to the overlying saline surface water or fresh groundwater from the inland shallow, surficial aquifer. For example, dissolved nitrogen in the plumes is predominantly found in reduced forms (i.e., ammonia and organic nitrogen. Furthermore, the plumes have brackish salinities indicating mixing between fresh, inland groundwater and saline surface water (i.e., surface water recirculation).

In nearby estuaries including Mobile Bay and Saint George Sound, seawater recirculation through nutrient-rich sediments is a significant source of groundwater nutrient loading (Santos et al., 2009; Beebe and Lowery, 2018). However; a history of nutrient loading from various point and non-point sources including chemical fertilization, onsite wastewater treatment, livestock waste, and centralized wastewater effluent disposal to groundwater in Southern Baldwin County has likely also contributed to elevated nutrient concentrations in the shallow aquifers (Dowling et al., 2004; Murgulet and Tick, 2008). The dynamic geochemical and physical conditions near the point of discharge obfuscate the source of groundwater nutrients entering the lagoon and also indicate the potential for chemical nutrient transformations between the land and sea that alter land-derived nutrients prior to discharge. Reactions including denitrification, mineralization, and ammonification may increase or decrease the influence of land use practices and management on nutrient loading to Little Lagoon.

With multiple potential sources of nutrients and a high potential for transformation during discharge to the surface, a strategic approach beyond routine nutrient sampling and analysis is needed to identify the sources of nutrients, especially nitrogen, to Little Lagoon. Therefore, the purpose of this study is to determine the sources of nutrients to groundwater surrounding Little Lagoon. The following work uses best available geochemical and hydrogeologic techniques to 'fingerprint' sources of nutrients in Little Lagoon and the surrounding surficial aquifer. However, these techniques are not without limitations given the ranges of uncertainty encountered during any hydrogeologic investigation. Therefore, results are interpreted with the express purpose of eliminating rather than confirming possible sources of nutrients within the Little Lagoon watershed.

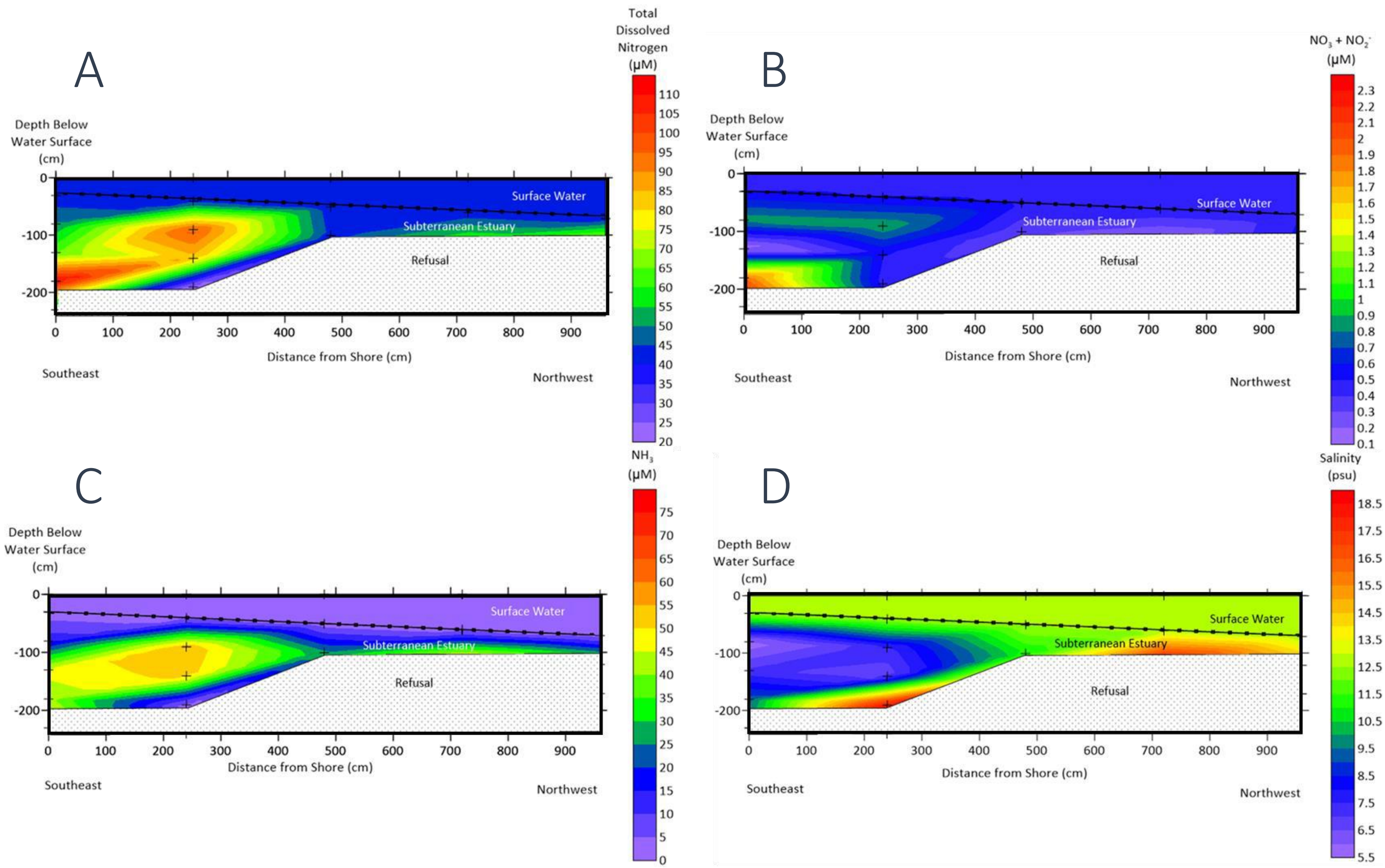

Figure 2 – Submarine groundwater geochemistry cross-sectional profiles collected at the point of discharge into Little Lagoon. A plume of nitrogen-rich (A), brackish (D) groundwater extending from the shore (bottom left of each profile) toward the surface water (top of each profile) is clearly evident. The plume is dominated by reduced nitrogen, especially ammonia (C), while nitrate concentrations are minimal (B).

Groundwater Sampling

Sampling locations

Groundwater samples were collected throughout the Little Lagoon watershed along a gradient of land use activities ranging from natural forest to heavy commercial residential and development (Figure 3). Samples were collected from four groundwater sources: (1) existing shallow monitoring wells installed by previous researchers and the Geological Survey of Alabama, (2) shallow monitoring wells installed during this project, (3) private irrigation wells, and (4) temporary, direct-push piezometers (i.e., SedPoints) (Figure 4).

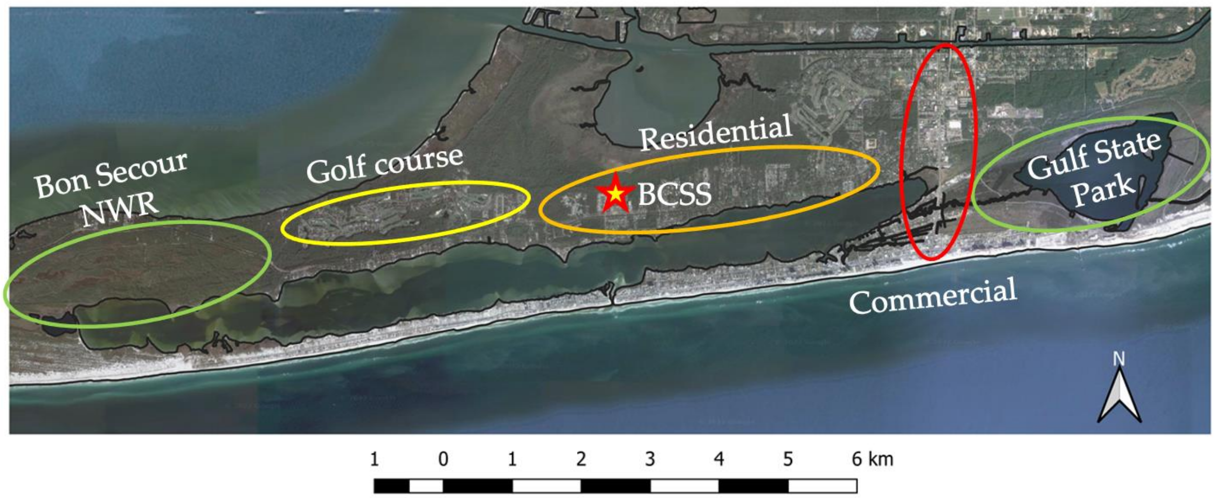

Figure 3 – Satellite imagery of Little Lagoon and surrounding land uses. A general gradient of development intensification exists along the shoreline of Little Lagoon from the western most end near Gator Lake in the Bon Secour National Wildlife Refuge to the eastern terminus close to Highway 59. The star in the center of the map indicates the location of the Baldwin County Sewer Services (BCSS) centralized wastewater treatment plant that relies on percolation ponds for effluent disposal to groundwater.

Figure 4 – Satellite imagery of the region surrounding Little Lagoon and groundwater sampling locations. A total of 33 groundwater samples were collected during the project.

Figure 5 – USA researchers stand next to newly installed monitoring wells. The hand auger can be seen in the foreground of the left picture and being held by one of researchers in the right picture. Casings were trimmed to approximately 15-20 cm above ground surface.

Monitoring well installation and sampling

Well construction details were generally unavailable for existing monitoring and irrigation wells, but measured and reported well bottom depths below ground surface indicate penetration no deeper than the surficial aquifer in all but one well on the southeastern shore of the Lagoon (i.e., sample I-8). Seven new monitoring wells were installed by the PI's team during the summer of 2021. Briefly, borings were drilled down below the water table using a hand auger until collapse inhibited further penetration. Then a well assembly consisting of 50 cm of 3.175-cm OD, PVC well screen coupled to PVC well casing was lowered into the open borehole (Figure 5). The annular space was backfilled using medium-grained sand to within 50 cm of the ground surface, and the remainder of the annular space was backfilled with cement to form a sanitary seal at the surface (Figure 6). Wells were developed using a combination of hand bailing and pumping.

Figure 6 – USA researchers trims the top casing of a freshly installed well to final height. The sanitary seal can be seen on the ground surrounding the casing. Fresh auger cuttings are preserved on the tarp.

Well sampling was conducted during the late summer and early fall of 2021. Typically, late summer is a "dry" hydrologic portion of the year; however, abnormally high precipitation persisted through late summer leading to wet conditions. Samples were collected after purging stagnant water until explanatory parameters reached near steady-state. In monitoring wells, purging was accomplished using a hand-held peristaltic pump. For private irrigation wells, existing infrastructure was used (Figure 7).

Additional purging was conducted at irrigation wells to facilitate pump cycling and basin flushing prior to any sample collection.

Collected samples were immediately analyzed for explanatory parameters (e.g., pH, dissolved oxygen, temperature, electrical conductivity, etc.) in the field using a Hanna multiparameter probe. 125 mL of each sample was filtered in the field using a glass fiber filter (Whatman GF/C, 1.2 µm) into a clean Nalgene sample bottle and transported on ice to the laboratory for further processing.

Figure 7 – Typical irrigation well infrastructure. All home owners reported using the same drilling service (Alm's Pump Service Inc.), and drilling records posted online suggest installation depths within the shallow, surficial aquifer for all but one well. Water samples were collected from the well-head spigot following purging.

Temporary Piezometer Installation and Sampling

Shallow groundwater samples were also collected at select residential locations using a temporary, drive-point piezometer apparatus (MHE SedPoint). Briefly, 6.25-mm OD polyethylene tubing with a terminal stainless-steel point and 5-cm of perforated screen was inserted into a hollow, 2.5-m stainless-steel installation rod and driven into the subsurface, below the water table using a slide hammer (Figure 8). The stainless-steel rod was carefully removed, leaving the screened polyethylene tubing in place. A peristaltic pump was used to draw shallow groundwater to the surface for explanatory parameter analysis using a multiparameter probe. As with well samples, 125 mL of each sample was filtered into a clean Nalgene bottle and transported to the lab on ice for further processing.

Groundwater Seeps and Canals

A few groundwater seeps and groundwater-fed canals were opportunistically sampled from roadside culverts within the Brigadoon subdivision (Figure 9). One seep was visually identified during a road-side inspection as groundwater emerging from the bank of a man-made drainage canal during irrigation well sampling in October. Others were identified after discussions with property owners in the Brigadoon subdivision and sampled later during January of 2022. Samples collected from either seeps or culverts were collected under dry antecedent conditions (i.e., no precipitation within the preceding 7 days) to ensure baseflow (i.e., groundwater) was the source of water. Samples were collected by hand and immediately analyzed for explanatory parameters. As with other samples, 125 mL of each sample was filtered into a clean Nalgene bottle and transported to the lab on ice for further processing.

Figure 8 – (Left) USA researchers pose with the piezometer installation rod, slide hammer, and peristaltic pump. The planted polyethylene piezometer (small tube) is located just below the pink flag in the center of the picture. (Right) Polyethylene piezometer and steel installation rod shortly after planting with slide hammer.

Figure 9 – (Left) Groundwater seep and manmade drainage canal in a vacant lot on the corner of Brigadoon Trail and Lagoon Winds Drive. The seep can be seen emerging from the bottom right corner of the photograph. (Right) Manmade drainage canal sampled along Brigadoon Trail.

Nutrient Analyses

Sample Processing and Analysis

Samples were transported from the field to the laboratory within 12 hours and filtered to 0.7 µm using Whatman GF/F filters. Nutrient analyses were either conducted within 48 hours of sample collection, or samples were stored in a deep freezer for later analysis (maximum hold time at refrigerated temperature was less than 48 hours).

All nutrient analyses were conducted at the University of South Alabama main campus Hydrogeology Laboratory. Nitrite, nitrate, total dissolved nitrogen, reactive phosphorous, and total dissolved phosphorous were analyzed using Hach TNTplus vial tests and a Hach DR3900 spectrophotometer when measured salinities were less than 0.5 ppt. To avoid ion interference, samples with salinities of 0.5 ppt or higher were analyzed using standard colorimetric methods (APHA, 2018) with stock reagents prepared daily in the lab along with matched matrix calibration standards and blanks. Ammonia was analyzed using an ammonia ion selective electrode (APHA, 2018). Dissolved organic nitrogen was calculated as the difference between total dissolved organic nitrogen and inorganic nitrogen species (i.e., nitrite, nitrate, and ammonia).

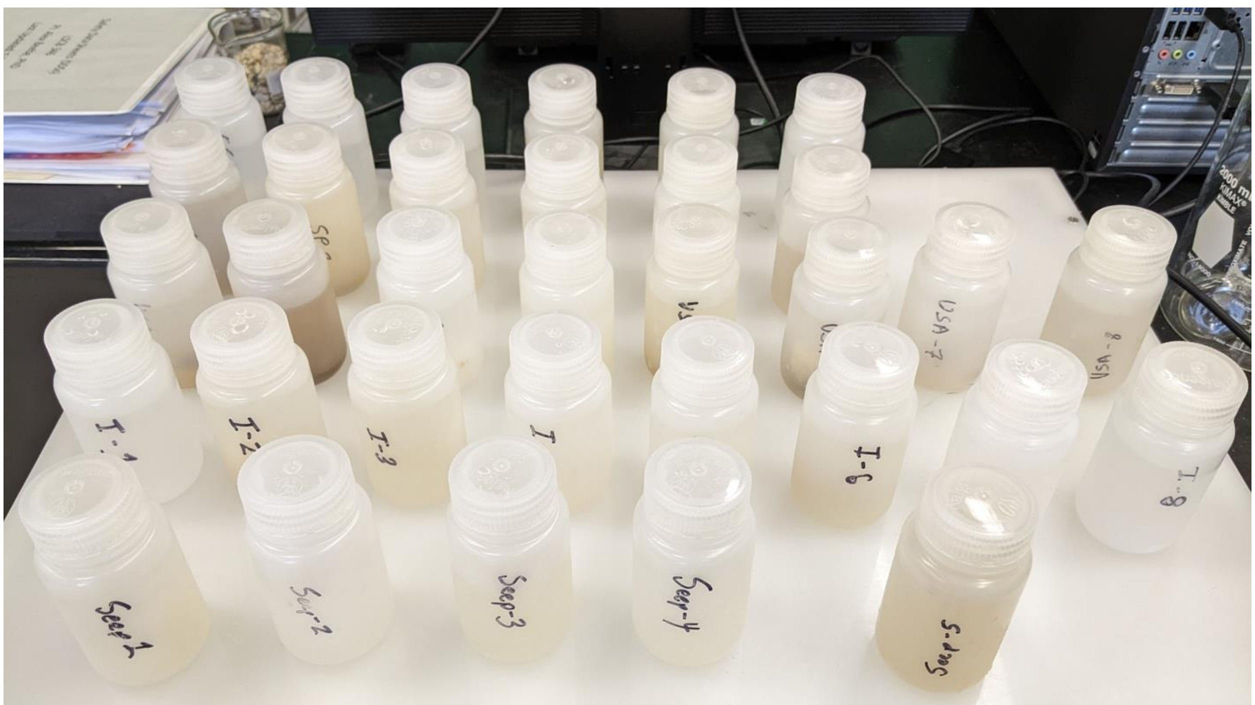

Figure 10 – Groundwater samples thawed prior to preparation for stable isotope analysis. Brown, tannin discoloration was noted in the shallow samples collected close to the shore of Little Lagoon.

Dissolved Nitrogen Spatial Trends and Hotspots

Total dissolved nitrogen concentrations in groundwater samples ranged from just below 1 mg-N/L in wells located within the Gulf State Park and Bon Secour National Wildlife Refuge to greater than 7 mg-N/L in a sample collected within the Brigadoon subdivision (Supplemental Data). Two anomalies containing elevated concentrations of total dissolved nitrogen were identified: (1) along the southeastern shore of the Lagoon close to Highway 59 and (2) around the Brigadoon subdivision close to the BCSS wastewater treatment plant (Figure 11). Elevated concentrations are defined as concentrations greater than 1 standard deviation above the mean of all samples (~ 3.5 mg-N/L).

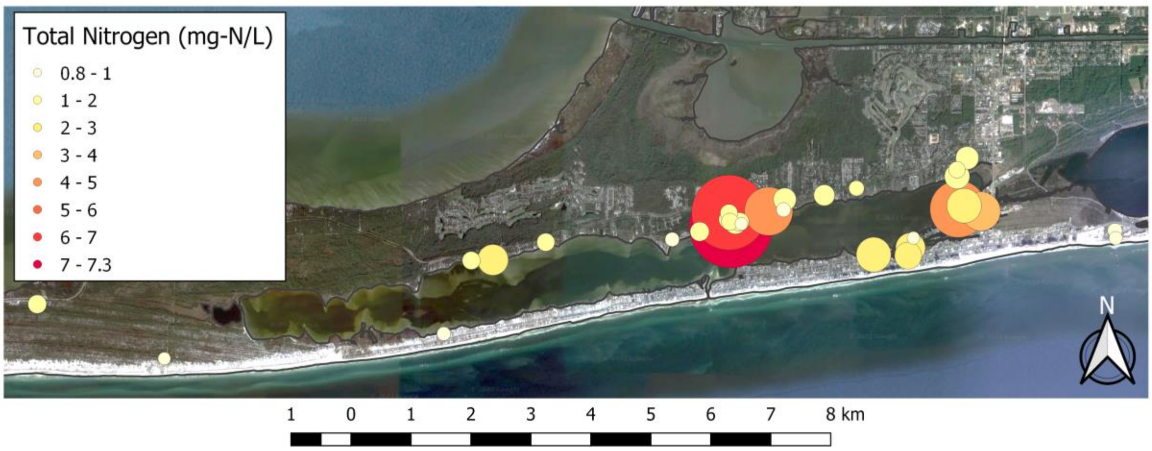

Figure 11 – Total dissolved nitrogen concentrations in groundwater samples. Circle sizes scale to concentration (i.e., larger circle = higher concentration). Two anomalies of elevated total dissolved nitrogen concentrations were noted: (1) on the southeastern shore of the Lagoon near Highway 59 and (2) around the Brigadoon subdivision near the BCSS wastewater treatment plant.

There were a few differences between the two dissolved nitrogen anomalies. The anomaly on the southeastern shore was dominated by reduced forms of dissolved nitrogen (i.e., ammonia and dissolved organic nitrogen), whereas the anomaly around the Brigadoon subdivision near the BCSS wastewater treatment plant was dominated by both oxidized and reduced forms of dissolved nitrogen (e.g., nitrite, nitrate, ammonia, and dissolved organic nitrogen) (Figures 12-14). Secondly, the southeastern shore anomaly was spatially consistent (i.e., concentrations in adjacent samples were similar) in contrast to Brigadoon subdivision where some wells contained below average concentrations (i.e., less than 2 mg-N/L) and others contained elevated concentrations (i.e., greater than 4 mg-N/L).

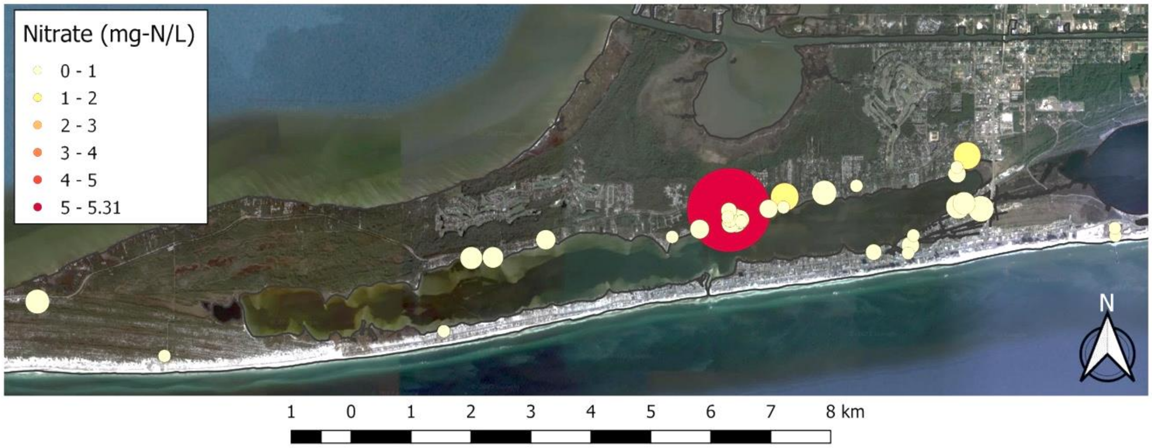

Figure 12 – Nitrate concentrations in groundwater samples. Concentrations were generally at or below 1 mg-N/L in all samples except for a single sample collected in the Brigadoon subdivision from a residential property with recent fertilizer usage.

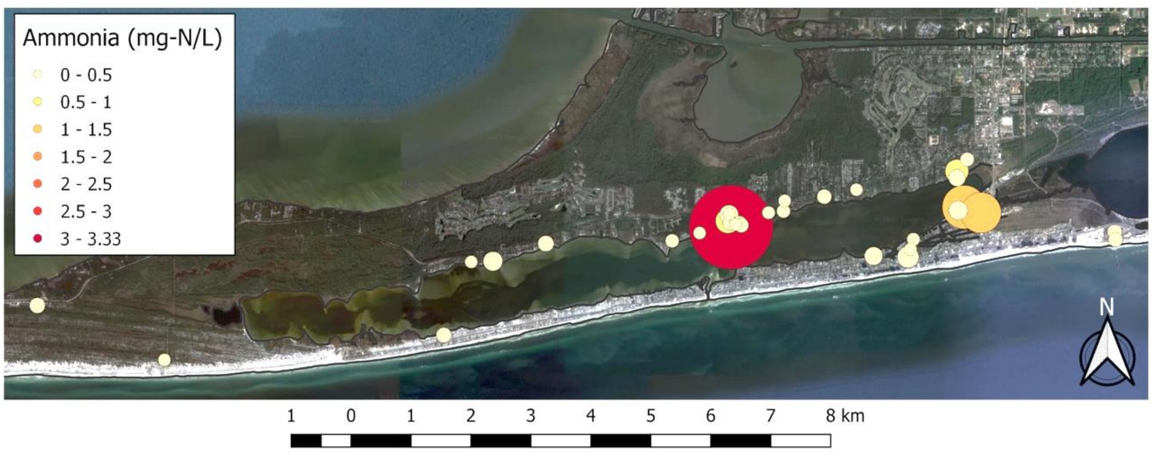

Figure 13 – Ammonia concentrations in groundwater samples. Elevated ammonia concentrations were observed in both anomalies.

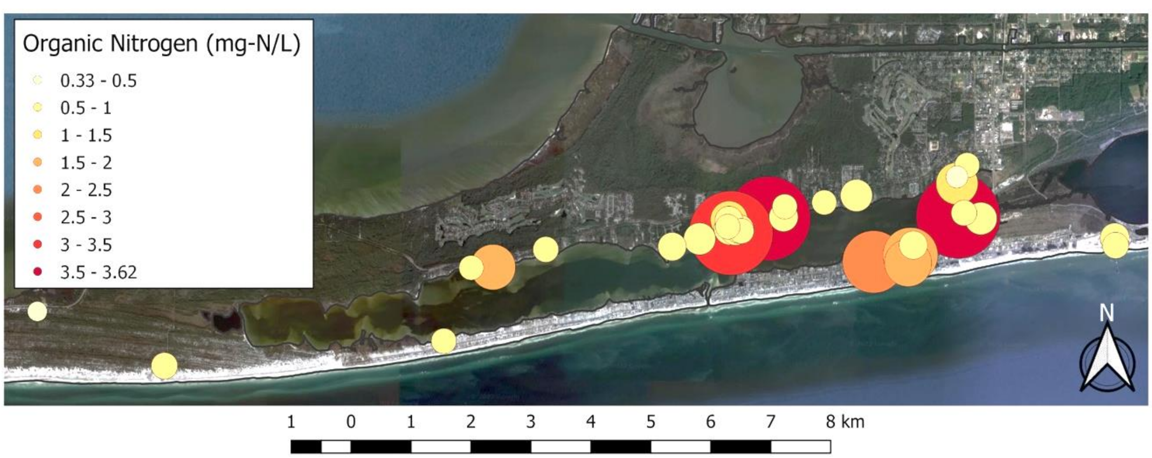

Figure 14 – Dissolved organic nitrogen concentrations in groundwater samples. Dissolved organic nitrogen concentrations were observed in both anomalies.

Nitrogen forms do not provide sufficient evidence to discriminate potential sources. However; previous groundwater studies conducted in Mobile and Baldwin counties have attributed reduced forms of nitrogen to remineralized and partially decayed soil organic material (Beebe and Lowery, 2018; Montiel et al., 2018). Oxidized forms of nitrogen have been attributed to chemical fertilizer applications (Murgulet and Tick, 2009).

Land use applications near both of the anomalies provide additional evidence and suggest possible sources. For example, fertilizer and onsite wastewater effluent disposal are possible sources of dissolved nitrogen to groundwater at both residential and commercial properties. Property owners were surveyed prior to groundwater sampling to document previous fertilizer applications and wastewater management (i.e., onsite vs centralized collection). No sampled properties are reliant on septic systems for onsite wastewater management, and only two sampled sites have a recent history of fertilizer application. Of the two sampled properties with a history of fertilizer application, one had elevated total dissolved nitrogen, dissolved organic nitrogen, and nitrate concentrations. However; both fertilized properties were located within 400-600 m of BCSS effluent disposal percolation ponds. These unlined percolation ponds receive treated effluent from the BCSS wastewater treatment plant which recharges directly to the surficial aquifer.

The wastewater treatment plant is permitted to dispose effluent treated to a maximum nitrate concentration of 10 mg-N/L, which is well above the highest total dissolved nitrogen concentration measured in groundwater samples during this study. The permitted concentration limit is presumably based on the USEPA drinking water maximum contaminant level (MCL) for nitrate which can contribute to methemoglobinemia in infants. However; the drinking water MCL does not consider possible ecological effects on receiving aquatic, estuarine, and marine systems – namely eutrophication. Furthermore, there are no criteria for other forms of dissolved nitrogen which may contribute to eutrophication, including ammonia and dissolved organic nitrogen. Therefore, these additional nitrogen species are not monitored in treated effluent although they could also contribute to the Brigadoon subdivision groundwater nitrogen anomaly.

Due to the overlapping spatial ranges of possible sources, an additional discriminatory analysis was necessary. Therefore, subsamples were prepared and analyzed for stable nitrogen and oxygen isotope ratios (See Stable Isotope Analyses section).

Dissolved Phosphorous Trends and Hotspots

Reactive and total dissolved phosphorous concentrations were below detectible limits in the majority of groundwater samples. However; there was one single anomaly of elevated phosphorous concentrations (i.e., greater than 1 mg/L as phosphate) located within the Brigadoon subdivision near the BCSS wastewater treatment plant (Figures 15 and 16). Both reactive and total dissolved phosphorous concentrations within the anomaly were as high as 5 mg/L as phosphate. There was very little difference between reactive and total dissolved phosphorous concentrations suggesting that total dissolved phosphorous is in the reactive, orthophosphate form, which is especially bioavailable to plants and algae.

Figure 15 – Total dissolved phosphorous concentrations in groundwater samples (mg/L as phosphate). Reactive phosphorous concentrations (not shown) are similar. One anomaly containing elevated phosphorous concentrations was observed in the Brigadoon subdivision in close proximity to the BCSS wastewater treatment plant effluent disposal percolation ponds.

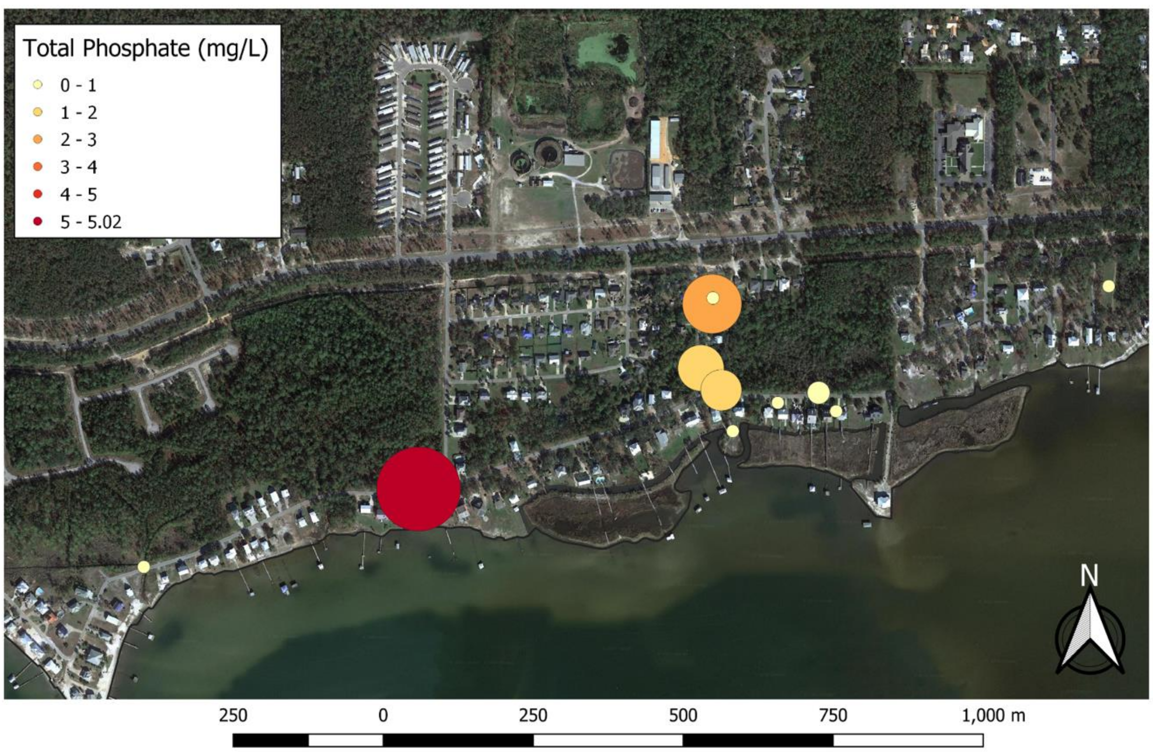

Figure 16 – Closeup of total dissolved phosphorous concentrations in groundwater from the Brigadoon subdivision. Dissolved phosphorous concentrations were highest in close proximity to the BCSS wastewater treatment system and associated effluent disposal percolation ponds.

Possible sources of phosphorous to groundwater include fertilizer application, animal waste, wastewater effluent disposal (onsite or centralized), desorption from soils, and dissolution of natural occurring geologic minerals. Given the land use activities surrounding the groundwater phosphorous anomaly, fertilizer application and wastewater effluent disposal are the two most likely sources. As mentioned in the subsection above (See Dissolved Nitrogen Spatial Trends and Hotspots), property owners were surveyed to document past fertilizer applications and wastewater management prior to groundwater sampling. No sampled properties are reliant on onsite wastewater treatment, and only two sampled properties have a recent history of fertilizer application. Of these two properties, neither had detectable concentrations of either reactive or total dissolved phosphorous. Spatial and land use evidence therefore suggests that the BCSS effluent disposal percolation ponds are the most likely explanation for the phosphorous anomaly. However; fertilizer application to sites adjacent to those sampled cannot be refuted as a possible source.

Stable Isotope Analyses

Theory

Stable isotope ratios for both nitrogen and oxygen change in predictable ways in the atmosphere and hydrosphere allowing for “fingerprinting” of possible nitrogen sources in groundwater. For example, nitrogen in manufactured, chemical fertilizers is typically sourced from “light” atmospheric nitrogen depleted in the heavier ^{15}N stable isotope. In contrast, nitrogen from animal waste and wastewater tends to become enriched in ^{15}N or “heavy” nitrogen as lighter ^{14}N is preferential lost to volatilization especially as organic nitrogen is converted to ammonia during remineralization. This difference in isotopic composition (i.e., weight) can be detected in nitrogen species found in groundwater samples and used to further discriminate potential sources.

Stable Isotope Preprocessing

Subsamples of ten groundwater samples were filtered to 0.2 µm using pressure filtration, acidified using concentrated hydrochloric acid, and placed in amber, non-reactive glass bottles prior to being shipped to a commercial stable isotope facility (Beta Analytic, Miami, FL) for stable nitrogen and oxygen isotope analysis. Given the low concentrations of nitrate generally found in groundwaters surrounding Little Lagoon, only six of these samples had sufficient concentrations for stable isotope analysis.

An additional 18 subsamples from 17 samples (i.e., 1 duplicate) were filtered to 0.2 µm using pressure filtration and digested using an alkaline persulfate digestion to oxidize all forms of dissolved nitrogen (i.e., total dissolved nitrogen) to nitrate. The subsamples were then frozen and shipped overnight with icepacks to the Stable Isotope Facility at University of California Davis for stable nitrogen analysis via the bacteria denitrifier method. Because all forms of nitrogen including reduced forms were oxidized to nitrate, only stable nitrogen and not stable oxygen ratios from these digested samples give an indication or possible sources.

Nitrate Stable Nitrogen and Oxygen Isotope Ratios

Nitrate stable nitrogen isotope ratios ($\delta^{15}NO_3\text{-}N_{Air}$) for the six analyzed samples were all between -6 to 6 ‰ which is consistent with manufactured fertilizer (Kendell et al., 2007) (Figure 17). Other possible sources suggested by isotopic analysis include atmospheric, soil, and marine nitrogen. Processed wastewater typically has a nitrate stable nitrogen isotope ratio greater than 10 and as high as 35 ‰. The nitrate stable nitrogen isotope ratio data along with surrounding land use data suggest that the nitrate anomaly (Figure 13) is most probably not sourced from the BCSS wastewater effluent percolation pond, but rather from fertilizer and/or atmospheric sources. The highest groundwater nitrate concentration detected during sampling was collected from a property with a recent history of fertilizer application.

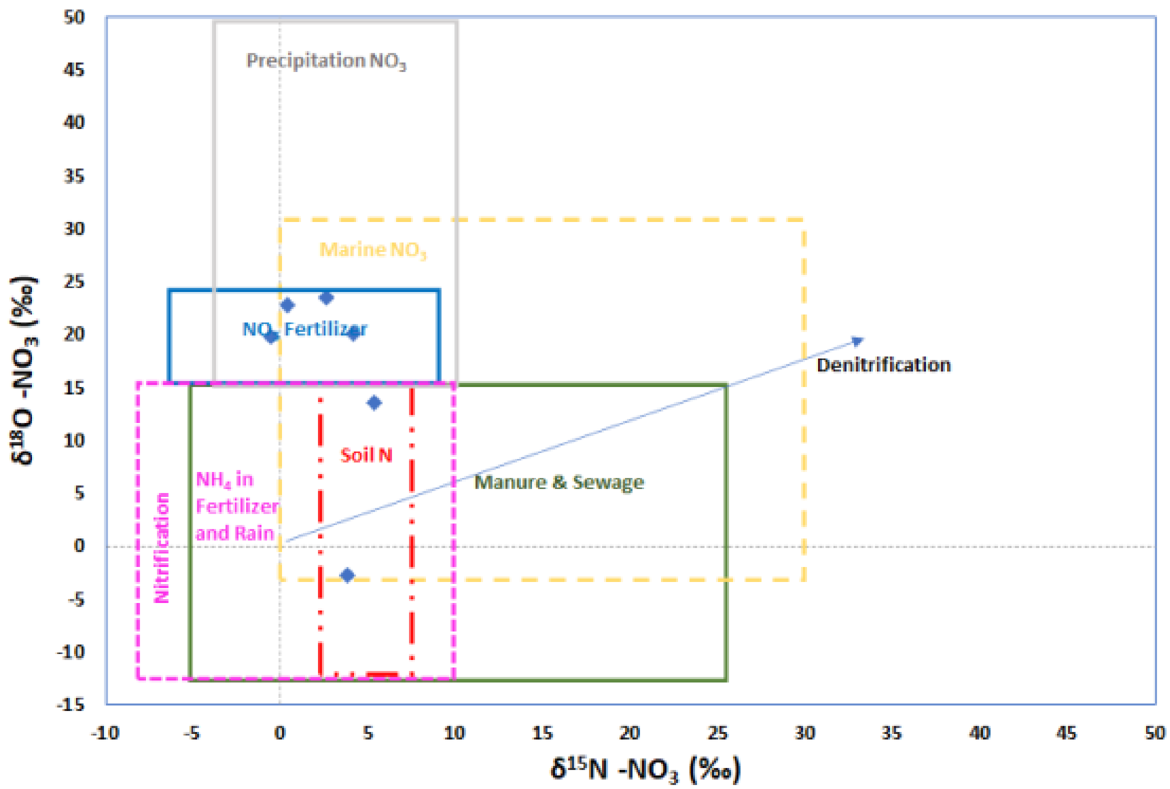

Figure 17 – Nitrate stable nitrogen and oxygen isotope ratios. The "light" nitrate stable nitrogen isotope signatures (i.e., less than 6 ‰) and surrounding land usages are suggestive of fertilizer and natural sources of nitrate to groundwater surrounding Little Lagoon.

Total Dissolved Nitrogen Stable Nitrogen Isotope Ratios

Total dissolved nitrogen stable nitrogen isotope ratios ($\delta^{15}TDN\text{-}N_{Air}$) were consistently between 5.6 and 10.7 ‰ which is just below the uppermost range of manufactured fertilizer (6 ‰) and just above the lowermost range processed wastewater (10 ‰) (Figure 18). Only one sample had a total dissolved nitrogen stable nitrogen isotope ratio below 6 ‰, and two samples had isotope ratios above 10 ‰. All samples had isotope ratios are squarely within the expected range for marine nitrogen (5 to 15 ‰)

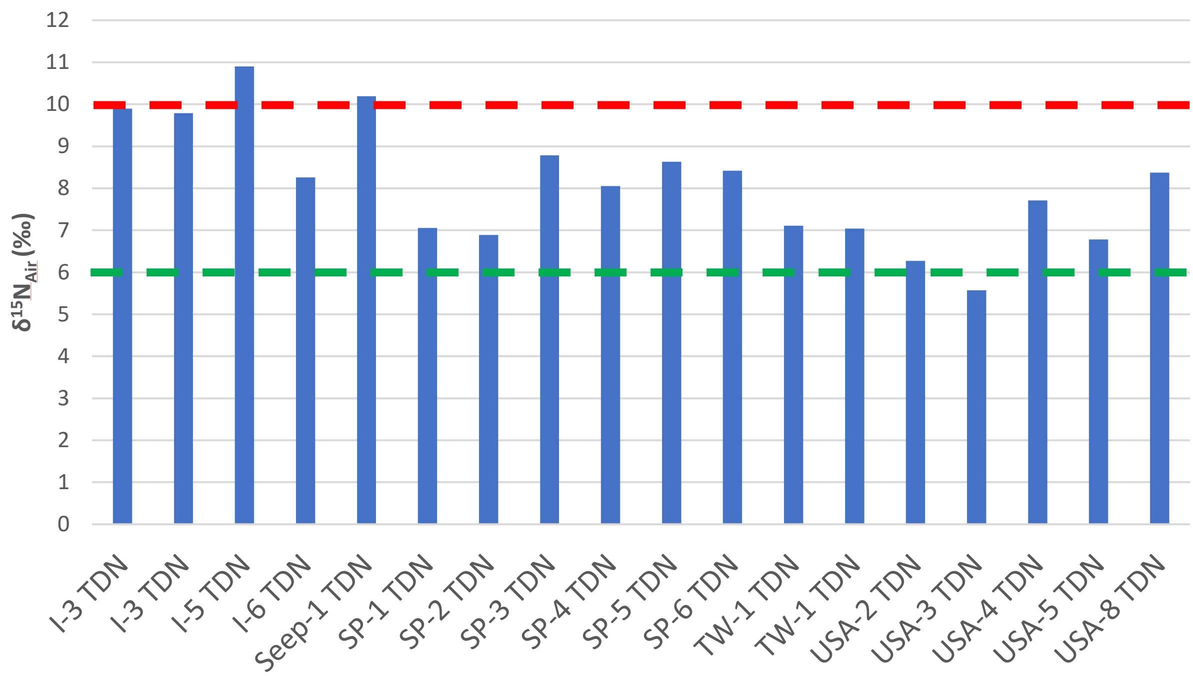

Figure 18 – Total dissolved nitrogen stable nitrogen isotope ratios. Dashed red line represents the lowermost expected value for processed wastewater, and dashed green line represents the uppermost expected value for chemical fertilizer.

The one sample with a total dissolved nitrogen stable nitrogen isotope ratio below 6 ‰ was collected from a residential property with the highest nitrate concentration measured during this study. As discussed previously, this residential property has a recent history of fertilizer application, indicating fertilizer as the likely source of total dissolved nitrogen for this one sample (See Nitrate Stable Nitrogen and Oxygen Isotope Ratios subsection above).

One of the two samples with total dissolved nitrogen stable nitrogen isotope ratios above 10 ‰ was collected from an irrigation well on the northeast shore of Little Lagoon (10.7 ‰), and the second was collected from a groundwater seep in the Brigadoon subdivision near the BCSS wastewater treatment plant (10.2 ‰) (Figure 9). Other samples from the Brigadoon subdivision had total dissolved nitrogen stable isotope ratios between 5.6 and 9.6 ‰. Even though these two samples were just within the expected range of processed wastewater, it is less likely that wastewater effluent is responsible for the heavy enrichment. Considering the higher ammonia concentrations associated with both of these samples (greater than 0.5 mg-N/L), it is more likely that in-situ volatilization is responsible for a slight enrichment of ^{15}N relative to the other samples.

A likely explanation is that most of the total dissolved nitrogen in groundwater samples is sourced from a mixture of decaying terrestrial and marine organic litter material in sediments. To illustrate, the highest total dissolved nitrogen concentration (7.3 mg-N/L) was measured in a sample collected from a newly installed monitoring well on the shore of Little Lagoon in the Brigadoon subdivision. Hand auger cuttings collected during well installation consisted of a mixture of black organic mud and peat (Figure 5

– left picture), indicating the presence of decaying plant material. Groundwater collected from the well throughout development and sampling was tannin stained and had a pungent, sulfurous odor, consistent with anaerobic decomposition. Other groundwater samples collected during the study, especially those collected closer to the shoreline, had a similar odor and appearance. Reduced forms of dissolved nitrogen, which dominated the nitrogen found in this study, have been attribute to decaying plant material in previously published groundwater studies from Mobile and Baldwin Counties (Beebe and Lowery, 2018; Montiel et al., 2018).

Terrain and Drainage Modeling

In an effort to further constrain the source of the phosphorous anomaly, drainage patterns in the Brigadoon subdivision were predicted using the 2014 Baldwin County digital elevation model from the USGS National Elevation Dataset (NED) and the Soil and Water Assessment Tool (SWAT+) (Figures 19-20). Subsurface flow directions typically follow surface drainage patterns in surficial aquifers located within temperate regions.

Although the drainage model does not account for road culverts, a dendritic drainage pattern containing the BCSS wastewater treatment plant effluent disposal percolation ponds appears to flow southward towards Little Lagoon. Surface water samples from groundwater-fed canals and tributaries were collected down-gradient of the wastewater treatment plant along Brigadoon Trail. Samples were also collected from adjacent culverts that drain areas not associated with the wastewater treatment plant. Elevated phosphorous concentrations only appeared in samples within the same drainage area that contains the BCSS wastewater treatment plant, lending further evidence to support the effluent disposal percolation ponds as the likely source of the anomaly (Figure 21). In addition, groundwater collected from an irrigation well, upgradient of the anomalous culvert samples also contained elevated concentrations of phosphorous.

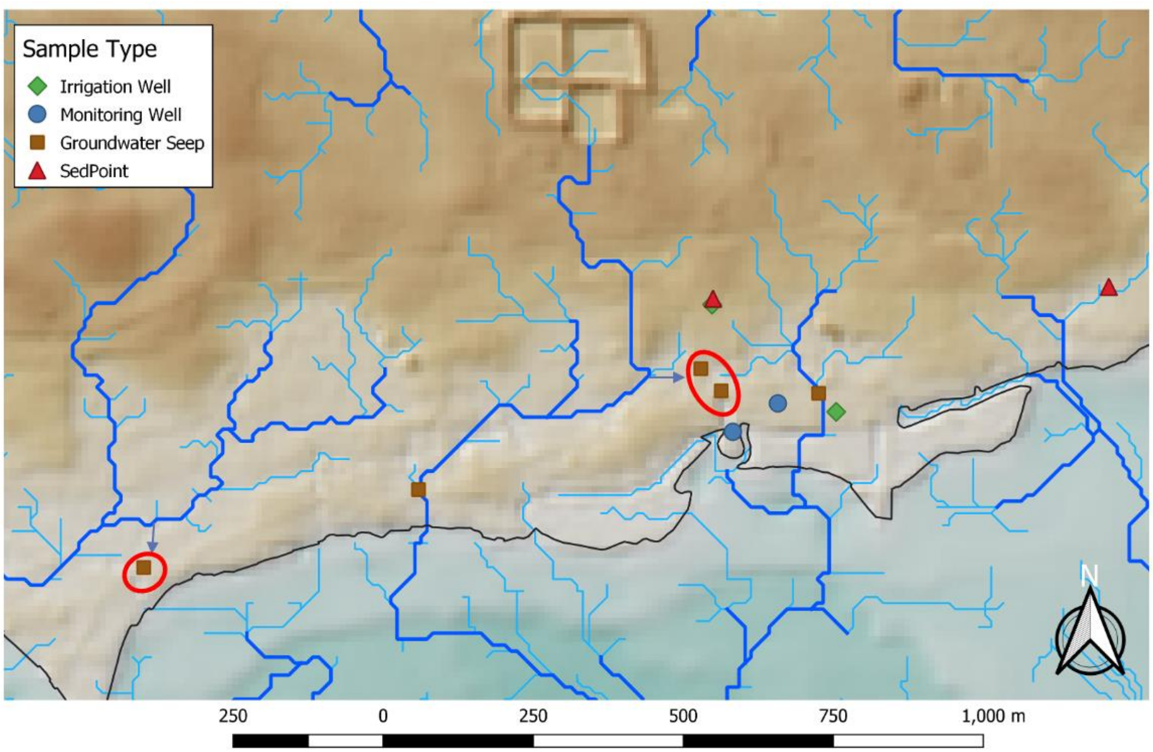

Figure 19 – Digital elevation model (DEM) and predicted surface drainage network from the Brigadoon subdivision and BCSS wastewater treatment plant. Percolation ponds are the rectangular depressions at the north, center portion of the map. Arrows and circles (added) indicate manmade drainages fed by roadside culverts.

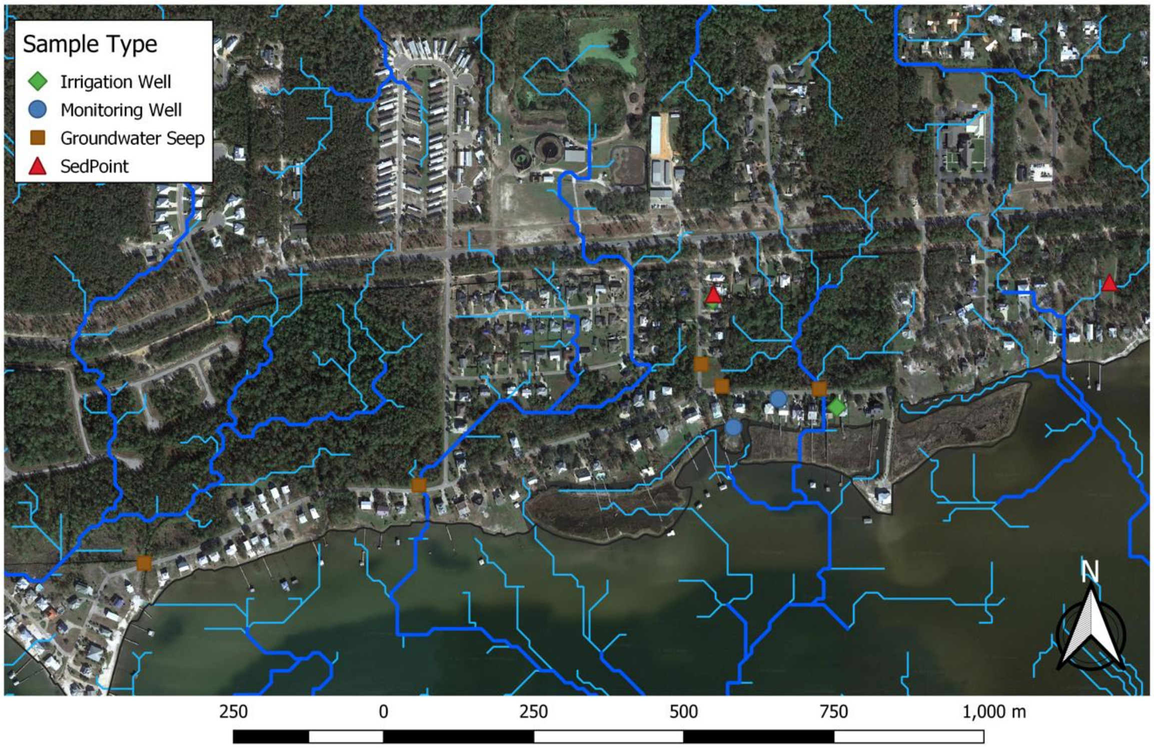

Figure 20 – Predicted drainage pattern superimposed on satellite photography.

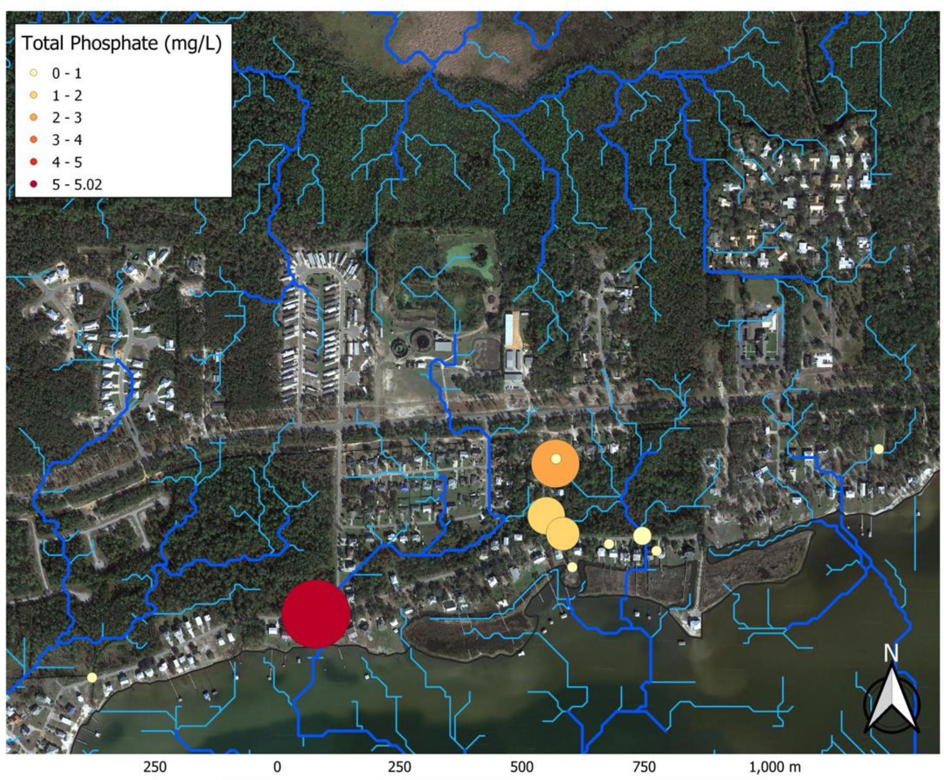

Figure 21 - Total dissolved phosphorous concentrations superimposed over the predicted drainage pattern. The phosphorous anomaly is constrained to the drainage down-gradient of the BCSS plant.

Nutrient Fate and Transport

Dissolved Nitrogen and Phosphorous Biogeochemistry

Both dissolved nitrogen and phosphorous can be subjected to numerous biogeochemical transformations and transfers between the land surface and point of subsurface discharge as submarine groundwater discharge. For example, dissolved nitrate is susceptible to reduction to innocuous nitrogen gas (N_2) through bacterially-mediated denitrification. Denitrification is favorable under reducing conditions, especially when dissolved oxygen concentrations are lower than 4.0 mg/L, oxidation reduction potentials (ORPs) are between -100 and 100 mV, and pH is greater than 6.0. Conversely, reduced forms of dissolved nitrogen (i.e., ammonia and organic nitrogen) are oxidized through nitrification under oxidizing conditions (e.g., dissolved oxygen great than 4.0 mg/L and oxidation reduction potential above 100 mV).

Phosphorous is less subject to chemical transformations, but is immobilized through mineral precipitation and surface adsorption onto soils and sediments. As a negatively-charged, polyatomic ion, phosphorous in the phosphate form (PO_4^{-3}) is readily adsorbed onto solid-phase iron oxyhydroxides that coat soils and certain aluminosilicate minerals (e.g., clays). While clay is a negligible portion of sediment composing the surficial aquifer, iron oxyhydroxides can form under oxidizing and basic conditions (Figure 22). In other words, oxidizing conditions are favorable for iron oxyhydroxide precipitation and subsequent adsorption of dissolved phosphate. Therefore, phosphorous in the phosphate form is possibly immobilized by iron under oxidizing conditions but not under reducing conditions. Since reactive phosphorous concentrations were similar to total dissolved phosphorous concentrations, total dissolved phosphorous is likely to follow this trend (i.e., immobilized under oxidizing conditions).

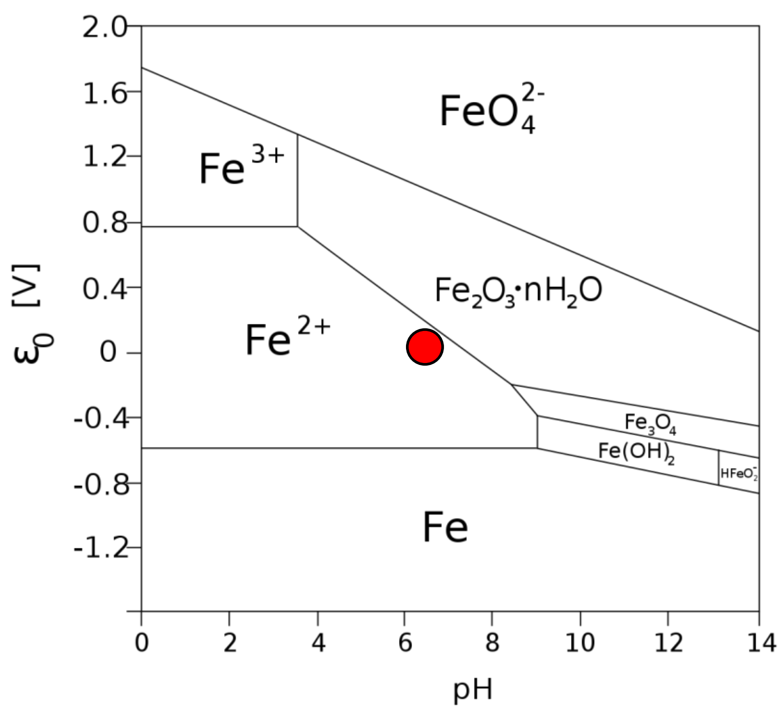

Figure 22 – Pourbaix diagram for Fe-O-H aqueous phase equilibrium products. Dissolved forms of iron (Fe) are indicated by charges. Red dot is groundwater average value from this study.

Aquifer Biogeochemistry

ORP, dissolved oxygen concentration (i.e., DO), and pH were generally indicative of more reducing and slightly acid conditions within the surficial aquifer surrounding Little Lagoon (Figures 22 and 23). In other words, nitrate is likely to be transformed to denitrification to nitrogen gas while phosphorous is less likely to be sequestered and immobilized by iron oxyhydroxide.

The biogeochemical conditions offer some explanation for the nutrient tends observed in groundwater samples collected during this study. For example, nitrate was undetectable in most samples, and only one sample collected from a residential site with a recent history of fertilization had a concerning concentration. It is likely that the aquifer biogeochemical conditions favor denitrification, and therefore, chemical transformation (i.e., removal) of nitrate. Conversely, these same conditions are less favorable for nitrification of the reduced forms of dissolved nitrogen (i.e., ammonia and dissolved organic nitrogen). In other words, reduced forms of nitrogen are less likely to be transformed and more likely to remain conservative and mobile in groundwater, and also more likely to contribute nitrogen to Little Lagoon.

A similar theme could explain the extent of the phosphorous anomaly in the Brigadoon subdivision near the BCSS wastewater treatment plant. Iron is less likely to precipitate as iron oxyhydroxide under the slightly acidic reducing conditions (Figure 22), leaving less potential for phosphate absorption and immobilization. Furthermore, the sandy lithology of the surficial contains very little clay for absorption. In other words, phosphorous, like reduced nitrogen, is likely to remain conservative and mobile in groundwater.

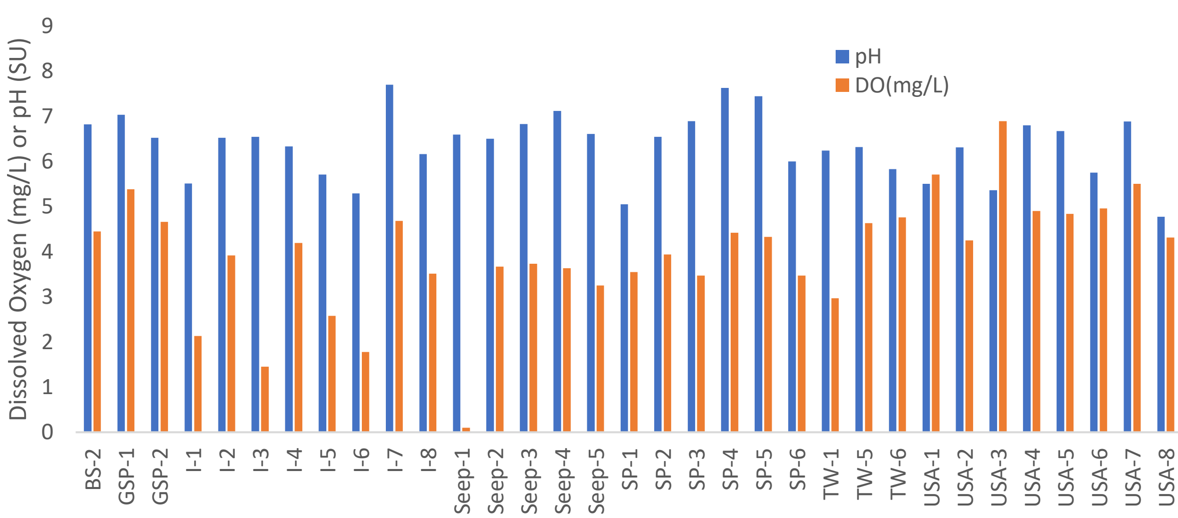

Figure 23 – Dissolved oxygen concentration and pH of groundwater samples. Average DO was 3.9 mg/L, and average pH was 6.4.

Subterranean Estuary Biogeochemistry

Several attempts were made to sample terrestrial, meteoric groundwater within the subterranean estuary in order to determine if additional biogeochemical transformations and transfers occur just prior to discharge to Little Lagoon (Figure 24). However; the unusual seasonal precipitation trend during spring of 2022 (i.e., drought) precluded the formation of any meteoric plume. Rather, the subterranean estuary exhibited signs of submarine groundwater recharge, or recirculation of surface water into the subsurface (Beebe et al., 2022). Salinity of subterranean estuary porewater was generally higher than both groundwater from the aquifer and also overlying surface waters. In other words, data collected from the subterranean estuary during this study do not provide any additional insight into nutrient biogeochemical transformations and transfers. However; given previous trends from Little Lagoon and other nearby estuaries in the Northern Gulf of Mexico (Beebe and Lowery, 2018) the subterranean estuary is likely to support reducing and slightly acidic conditions not dissimilar to the inland aquifer.

Figure 24 – SedPoint apparatus used for sampling the subterranean estuary. There was no evidence of terrestrial submarine groundwater discharge during spring 2022, and conditions were generally reducing and slightly acidic, not unlike the inland aquifer.

Conclusion

Two spatial anomalies containing elevated nutrient concentrations were revealed from the groundwater sampling: one on the southeastern shore of the Lagoon in an area of commercial and residential development and another on the northern, central shore around the Brigadoon subdivision downgradient of the Baldwin County Sewer Services (BCSS) wastewater treatment plant. The anomaly on the southeastern shore contained elevated total dissolved nitrogen, dissolved organic nitrogen, and ammonia. Stable nitrogen isotope analyses of persulfate digested subsamples (i.e., total dissolved nitrogen) suggests a natural source – most likely remineralized and partially decayed soil organic material. This finding is consistent with studies conducted in other nearby estuaries.

The second anomaly around the Brigadoon subdivision and BCSS wastewater treatment plant contained elevated total dissolved nitrogen, dissolved organic nitrogen, ammonia, nitrate, reactive phosphorous, and total dissolved phosphorous. Stable nitrogen and oxygen isotope analyses of nitrate subsamples suggest a mixture of fertilizer and natural sources of nitrate. Stable nitrogen isotope analyses of digested subsamples suggest that the reduced forms of nitrogen (i.e., ammonia and dissolved organic nitrogen) are from a natural source – consistent with the reduced dissolved nitrogen anomaly on the southeastern shore. There is no compelling evidence to suggest a wastewater source (onsite or centralized) of dissolved nitrogen to groundwater in the areas that were sampled.

The source of reactive phosphorous and total dissolved phosphorous in the anomaly around the Brigadoon subdivision and BCSS wastewater treatment plant is more difficult to discern as there is no reliable stable isotope analysis available to discriminate phosphorous sources. However, spatial as well as terrain and drainage modeling evidence suggests that the effluent percolations ponds used by the BCSS wastewater treatment plant for effluent disposal are the most likely source of the dissolved phosphorous anomaly.

Geochemical conditions within the surficial aquifer surrounding Little Lagoon and especially within the subterranean estuary are generally favorable for nitrate reduction and transformation via denitrification. However, these same conditions are less favorable for nitrogen oxidation, aerobic biodegradation, and phosphorous adsorption. Therefore, application of reduced forms of nitrogen (i.e., ammonia and dissolved organic nitrogen) and phosphorous to land surfaces within the Little Lagoon watershed warrants concern due to an increased risk of eutrophication. Additional monitoring of phosphorous in the vicinity of the wastewater treatment plant, and contingent on monitoring results, possible changes in wastewater treatment and disposal practices are likely needed to protect and preserve the quality of water and ecology in Little Lagoon.

Limitations

Our interpretations are based on most likely explanations from the data at hand. Although this study points to probably sources of nutrients in the groundwater surrounding Little Lagoon, there are some limitations that could be addressed to provide additional constraint. Samples were collected where the PI was able to gain access, and not necessarily where plumes could be detected. It is possible that additional sampling could reveal new nutrient anomalies. Furthermore, additional sampling may confirm (or refute) the BCSS wastewater effluent disposal percolation ponds as the source of the phosphorous anomaly.

There are also other techniques that could be used to study flow within the inland aquifer including tracer tests and numeric hydrogeologic modeling. Hydrogeologic models are commonly employed to investigate the impacts of spray fields used in Florida to dispose of treated wastewater effluent. These models are especially reliable for identifying areas of wastewater return flow (i.e., daylighting) which serve as priority areas for monitoring. Tracer testing is another technique used to identify flow pathways within aquifers; however, given the lower predicted velocity of groundwater within the surficial aquifer, any tracers tests should be preceded by hydrogeologic modeling to develop a robust tracer monitoring strategy.

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