

GROUNDWATER FLOW DYNAMICS AND CONTAMINANT TRANSPORT TO  
COASTAL WATERS UNDER LOW RECHARGE CONDITIONS: REGIONAL-SCALE  
STUDY OF THE AQUIFER SYSTEM UNDERLYING SOUTHERN BALDWIN COUNTY,  
ALABAMA

by

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A DISSERTATION

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## ABSTRACT

This study examined the influence of drought conditions and increased hydrological stresses on the groundwater system flow dynamics, submarine groundwater discharge, and nitrate transport and discharge to the Gulf of Mexico. The results of these studies demonstrate that current stresses on the aquifer have led to significant saltwater intrusion and or direct infiltration into fresh groundwater, especially within the upper aquifers of the region. The nitrate and chloride data analyses reveal the persistent presence of multiple nitrate impacted zones within the study area. Stable isotope data support the hypothesis that nitrate in the investigated aquifers originates from the nitrification of ammonium in soils from a mixture of sources ranging from fertilizer to sewer and/or manure and that denitrification, the breakdown of nitrates to nitrogen gas, is not significant in the investigated aquifer system. Furthermore, groundwater isotope data indicates that water in the aquifer system of the study area is most likely to have originated from precipitation and soil infiltration through relatively localized recharge and that the aquifer system in the study area is highly dynamic, experiencing mixing of recent recharged waters with older, ambient groundwaters. The presence of low residence times and the absence of denitrification reveal the oxic character of this system. As a proxy for a number of contaminant types, the groundwater flow and transport model was used to simulate nitrate transport in response to variable-density groundwater flow. The simulation results indicate that in the investigated aquifer system complexities arise because groundwater flow dynamics and contaminant transport are additionally influenced by density variations that can occur from the incursion of saltwater.

The model predicts that the Beach Sand and Gulf Shores Aquifers will be impacted by severe saltwater intrusion whereas the deeper 350 and 500-Foot Aquifers will experience no saltwater intrusion for the entire simulation period. Consequently, nitrate discharge to the Gulf of Mexico originates from the lower part of the aquifer system through submarine groundwater discharge. This research will serve as a tool which may be applied to other similar coastal systems for more effective management strategies.

## DEDICATION

This work is dedicated to the most important people in my life, whom I neglected and sacrificed throughout my PhD course: to my daughter, Ioana Murgulet (a source of joy and comfort), to my husband, Valeriu Murgulet, and to my parents, Sava and Iliana Leon.

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## INTRODUCTION

Contamination of ground water due to salt water intrusion as well as due to nutrients has become a major concern for coastal communities which rely on ground water as their principal source of drinking water. Groundwater represents an important source of nutrients and other contaminants that affect the ecology of the estuaries and coastal fresh water bodies (Weiskel and Howes 1992; Portnoy and others 1998; Nowicki and others 1999). Nitrogen (N), phosphorous, and suspended sediment are just a few of the contaminants that can contribute to the deterioration of water quality in coastal zones. The contaminants coming from various sources can be transported to surface waters by surface runoff and ground water discharge. Multiple studies indicate that the concentration of groundwater contaminants increases with increasing housing density. Thus, the increasing population of the coastal zones in the United States may substantially contribute to the ground water contamination thereby degrading the ecological health of the coastal waters and ocean.

With increasing development and tourism in these regions both ground water resources and environmentally sensitive areas such as coastal wetlands and ecological coastal habitats will be at risk. The protection of ground water resources from salt water intrusion, nutrient contamination and overdraft, has become and will continue to be a critical concern in these areas.

The role of groundwater in delivering contaminants to coastal waters has become an area of growing interest and of high concern. Submarine groundwater discharge (SGWD) is a potentially important source of nutrients to the coastal ocean.

As a result it is important to understand and quantify the status of groundwater flux to the ocean and to the coastal surface waters as well as the groundwater nutrient flux associated with the freshwater/saltwater transition zone. Flow paths and residence times of groundwater in the aquifer system and within the transition zone provide information on groundwater fluxes and contaminant fate. Since both the saltwater intrusion, particularly seawater, and the nutrient contamination of drinking water and coastal surface waters problems are mainly the imprints of anthropogenic practices and negative water balance, it is essential to evaluate their long-term effects on the groundwater and surface water quality. These factors can compromise ground water quality due to elevated levels of salinity, rendering the water supply unsuitable for various purposes such as drinking water. In addition, these changes in conditions may have impacts on the quality of water discharging into coastal waters due to ion exchange and other reactions between the aquifer solids and the saline water. Nutrient fluxes from groundwater to the ocean are dependent on groundwater velocity near the shoreline. Therefore, nutrient input, aquifer characteristics, fluctuations of sea level caused by waves and tides and groundwater table fluctuations with increasing groundwater demand and precipitation are factors contributing to the nitrate ( $\text{NO}_3^-$ ) flux to the shoreline and saltwater intrusion to the coastal aquifers.

The research area (1,626  $\text{km}^2$ ), located in Southern Baldwin County, Alabama, South of Interstate 10, is bounded to the South by the Gulf of Mexico and to the west, Southeast and East by Mobile Bay, Perdido River and Perdido Bay respectively. Areas vulnerable to salt water encroachment such as Fort Morgan Peninsula, Gulf Shores, Orange Beach and Perdido Beach are part of the investigated region. The coastal regions of Baldwin County are characterized by a continuously growing economy and rapid rate of development. The economy of the county is based primarily on tourism, agriculture, fishery, and seafood processing industries. Agriculture

makes up a large percentage of the land use/land cover within the study area. Recreational land use in the region includes community recreational facilities (i.e., resorts, hotels, tourist attractions, and dining establishments) and golf courses.

With these documented expansions of population and industrial development (i.e., cities and coastal areas), demands on water use in Southern Baldwin County have increased over the last few decades from  $2.7 \times 10^4$  m<sup>3</sup>/day to  $1.6 \times 10^5$  m<sup>3</sup>/day ( $2.7 \times 10^7$  L/day to  $1.6 \times 10^8$  L/day) between 1966 and 1995 (Reed and McCain 1971; Robinson et al. 1996a).

### **Statement of the Problem**

Saltwater intrusion and nitrate (NO<sub>3</sub><sup>-</sup>) contamination of groundwater and surface water are major problems for coastal aquifers. The principal causes are anthropogenic activities, lack of management and overdevelopment of water resources. With increasing development and tourism in coastal regions both ground water resources and environmentally sensitive areas such as coastal wetlands and ecological coastal habitats will be at risk. Protection of ground water resources from seawater encroachment and nutrient contamination is a real concern for coastal communities due to the impacts associated with increasing population, development, agriculture and tourism in these highly desirable coastal regions. In addition, predictions of increasing sea level and increased frequency and intensity of tropical storms and hurricanes in the region may exacerbate the saltwater intrusion problem over the long term.

In recent years, Baldwin County has experienced some of the most rapid growth in public and private sectors, ranking third among all counties within the state of Alabama. As a result, decreasing quality of groundwater and surface water due to extensive agricultural practices, and urban and residential expansion, has become a concern in the region. Groundwater and surface water resources in Southern Baldwin County, Alabama are vital to support the rapidly growing

population of the area and the evolving economy within the region, and to ensure that environmentally-sensitive ecosystems such as coastal estuaries and wetlands are preserved in the region. Growing population, tourism, and industry is dependent upon the quality and quantity of the water resources and health of the ecosystem within the region. Continued and extensive residential and agricultural development of near-shore areas in Southern Baldwin County is leading to increased inputs of  $\text{NO}_3^-$  from fertilizers, wastewater and septic tanks to groundwater, and as part of the hydrogeologic cycle, to the coastal waters and to the Gulf of Mexico (Valiela et al. 1990). Hence, anthropogenic contamination of the aquifer system in the form of high  $\text{NO}_3^-$  concentrations and saltwater intrusion from the Gulf of Mexico has become a real concern in this area.

The  $\text{NO}_3^-$  problem is most evident in the mobile form of  $\text{NO}_3^-$  and it is known to cause health problems in humans (Rajagopal & Tobin 1989) and contribute to the eutrophication of surface waters (Cooper 1993). Currently there is a lack of information and understanding of  $\text{NO}_3^-$  input to the aquifer system and transport to coastal waters in Alabama. Some of the major concerns of  $\text{NO}_3^-$  contamination/loading both to groundwater and surface water systems include health risk to humans through drinking water such as methemoglobinemia and potential carcinogenic effects, and detriment to the local ecosystems by adversely affecting a variety of marine and freshwater organisms such as fish and shrimp (i.e. seafood industry) and the health of wetlands which can be severely impacted by excessive plant and algal growth and constriction. A large majority of  $\text{NO}_3^-$  sources have anthropogenic origin and they are mostly confined to the same watershed and groundwater basin. In Southern Baldwin County, agricultural and residential application of fertilizers, sewage breakthrough, precipitation, and land application of animal

waste are some of the major sources of  $\text{NO}_3^-$ , the common form of N that infiltrates downward to the ground water.

The role of groundwater in delivering contaminants to coastal waters has become an area of growing interest and concern, in particular the discharge of excess nutrients to coastal ecosystems. Delineation of the extent of saltwater intrusion in the coastal aquifers not only plays an important role on water resources management, but helps understanding  $\text{NO}_3^-$  fate and flux to coastal ocean through SGWD and seawater cycling. Additionally, quantification of  $\text{NO}_3^-$  flux to coastal waters should account for the effect of density driven flow caused by the presence of saltwater intrusion.

### **Previous Work**

Although studies have been conducted in Baldwin County regarding the hydrogeology of the area, relatively little research has been conducted on locating the freshwater/saltwater interface and  $\text{NO}_3^-$  fate and flux to the coastal aquifers, surface water bodies in the region, and to the Gulf of Mexico. In addition, the influence of salinity on the nutrient flux and fate to the coast has never been approached.

Previous hydrogeological studies in the area include Gillett et al. (2000), Chandler *et al.* (1985) and Walter and Kidd (1979). The N stable isotopes approach to the  $\text{NO}_3^-$  sources identification has been used by several investigators to characterize the  $\text{NO}_3^-$  contamination problems in surface water and groundwater of many other regions (e.g. Kreitler 1975; Black and Waring 1977; Wolterink et al. 1979; Heaton 1986; and many others) but the technique has not been applied to Baldwin County. A previous study in Southern Baldwin County (Dowling et al. 2004) investigated and quantified  $\text{NO}_3^-$  flux to the Gulf of Mexico. The study concluded that groundwater discharge could have a high contribution to the nutrients loading to the Gulf of

Mexico. None of the previous studies examined the effects of  $\text{NO}_3^-$  /nutrient loading on local and regional aquifer systems and coastal surface water bodies (i.e. estuaries and wetlands). They also did not address the importance of the aquifer seawater cycling in identifying and quantifying  $\text{NO}_3^-$  fate and flux respectively.

The most recent studies in the region were conducted by Liu et al. (2007) and Murgulet and Tick (2007, 2008). Liu et al. (2007) investigated the current state of groundwater withdrawal from Fort Morgan Peninsula, producing a capture zone analysis for the area. Their results indicate that the area of Fort Morgan Peninsula has extensive cones of depression and is highly vulnerable to saltwater intrusion. Murgulet and Tick (2007, 2008) conducted an extensive regional saltwater intrusion and nitrate contamination assessment study that shows that ground water quality in Southern Baldwin County is being degraded in close proximity to the coast as a result of elevated chloride concentrations and further inland due to the presence of elevated nitrate in groundwater.

In Southern Baldwin County, agricultural and urban uses of fertilizers and sewage breakthrough are the primary sources that contribute to nutrient contamination of groundwater and surface water. Nitrate contamination may be a potential problem in some of the aquifers of Baldwin County, with nitrate levels in some wells exceeding regulatory drinking water standards (10 mg/L  $\text{NO}_3^-$  -N). Not only is this a concern for human health but groundwater discharge and surface-runoff of elevated  $\text{NO}_3^-$  levels to coastal surface waters may adversely affect the ecological health of coastal wetlands, embayments, and estuaries. Therefore, it is imperative to identify sources of  $\text{NO}_3^-$  contamination/loading and to determine the status of groundwater quality for this area, in particular the extent of  $\text{NO}_3^-$  contamination in groundwater and discharge to coastal waters and the Gulf of Mexico. Besides the  $\text{NO}_3^-$  problem, the salinization of the

coastal aquifers in this area has been proven to be a problem and to affect the freshwater resources and thus the economy and development.

### **Objectives and Importance of Work**

The objectives of this study are part of a large scale effort to 1) assess the extent of  $\text{NO}_3^-$  contamination and saltwater intrusion in the aquifers beneath Southern Baldwin County; 2) identify the source zones and fate (e.g. nitrification/denitrification) of  $\text{NO}_3^-$  in groundwater and coastal surface waters 3) determine  $\text{NO}_3^-$  loading to coastal surface waters from groundwater; 4); determine the primary contributions (i.e. groundwater versus surface water) of  $\text{NO}_3^-$  input to the coastal surface waters; 5) determine flow rates and residence times in the aquifer system and within the transition zones; and 6) construct a two-dimensional groundwater model as a way of simulating the extent of  $\text{NO}_3^-$  contamination in coastal aquifers accounting for the effect of density driven flow caused by the presence of saltwater intrusion.

Additionally, as part of the objectives of this research, a detailed user-friendly geographic information system (GIS) database was developed for the study area that integrated all of the collected data for easy update, visual display, and analysis. Tools such as these are critical for developing cost-effective aquifer management plans and protecting ecologically sensitive surface water bodies such as coastal estuaries and wetlands in the region.

The need for further studies in this area is critical to ensure that the water resources and ecology of the region are preserved. The research proposed herein is therefore an ideal continuation and expansion upon the most recent studies in the area. To better understand the current state of  $\text{NO}_3^-$  contamination in groundwater and surface water, contributions of  $\text{NO}_3^-$  loading to the Gulf of Mexico and to the coastal surface waters (estuaries and wetlands), and the fate of  $\text{NO}_3^-$  in these systems will require studies such as the one proposed herein. These studies

are vital for understanding links and exposure of  $\text{NO}_3^-$  to humans, assessing the impacts of  $\text{NO}_3^-$  on the local and regional ecology, and developing integrative management strategies for  $\text{NO}_3^-$ -N contamination and loading (as well as other contaminants) in the region.

This will be the first known study to assess  $\text{NO}_3^-$  fate and mass flux to surface waters using geochemical and modeling techniques. Furthermore, estimation of nitrate transport to coastal aquifers and surface waters accounting for density-difference between freshwater and seawater has never been approached in such matter and at such large scale and detail.

### **Summary of Findings and Relationships Among Research Themes**

This dissertation examines four major themes of groundwater flow and contaminant transport through a comprehensive regional-scale study of a coastal aquifer system in Southern Baldwin County, Alabama. The first major theme includes a study characterizing the extent and magnitude of saltwater intrusion within an aquifer system that is ever increasingly stressed due to rapidly growing population and associated demands on the groundwater resources from irrigation, agriculture, industrial, and water supply needs. This study demonstrates that current stresses on the aquifer have led to significant saltwater intrusion and or direct infiltration into fresh groundwater, especially within the upper aquifers of the region. Although there is likely significant vertical infiltration of high salinity water into the upper unconfined aquifer due to storm surges, it is clearly evident that saltwater intrusion is occurring in the region from chloride and salinity relationships measured in the deeper Aquifer A2 system.

The second theme investigates contaminant source identification, fate, and transport within a coastal aquifer system. This study specifically focuses on the origin of nitrate and the primary processes controlling the transport and fate of nitrate within the aquifer system and eventually discharging to coastal surface water bodies and the Gulf of Mexico. The findings of

this study indicate the presence of multiple nitrate impacted zones from a mixture of sources such as fertilizer and manure application and sewer breakthrough Isotope and geochemical data analyses reveal that the presence of nitrate was likely the result of mixed end-members with signatures ranging from fertilizer to sewer and/or manure.

The third major theme examines the groundwater flow dynamics and groundwater evolution through a coastal aquifer in order to determine the major processes controlling recharge, discharge, residence times, and mixing effects within the system and along major flow paths. This study implemented the use of multi-isotopes and geochemical parameters including radiocarbon and stable isotopes of carbon, hydrogen, and carbon. to determine and resolve some of the primary processes controlling recharge, groundwater flow and mixing in this system. This study led to the development of improved conceptual models of groundwater flow and transport within coastal aquifer systems and provided a detailed understanding of how contaminants may be influenced through such systems. These isotope studies validate the fact that the aquifer system in Southern Baldwin County is a highly dynamic system experiencing mixing of recent recharged waters with older, ambient groundwaters

The fourth major theme investigates groundwater flow and transport dynamics in a coastal aquifer system implementing the use of a coupled variable-density groundwater flow and transport model. SEAWAT, MODFLOW, and MT3DMS codes were used to understand the regional flow system within a coastal aquifer system by calibrating to observed hydraulic heads and comparing the results to what has been observed from the previous contaminant, multi-isotope, geochemical, and saltwater studies as a part of this dissertation research. As a proxy for a number of contaminant types, the groundwater flow and transport model was used to simulate nitrate transport, since extensive nitrate contamination was observed in the studied aquifer

system. Model results confirm several important observations: (a) nitrate discharge to the coastal waters decreases as the severity of saltwater intrusion increases (b) vertical gradients and mixing appears to be significant, and (c) canals such as the Intracoastal Waterway play an important role in diverting groundwater flow direction and contaminant transport and discharge to the Gulf of Mexico.

These studies are vital for understanding links and exposure of nitrate to humans, assessing the impacts of nitrate on the local and regional ecology, and developing integrative management strategies for nitrate contamination and loading (as well as other contaminants) in the region.

The work in articles 1, 2, 3, and 4 has been the subject of three technical reports to the Alabama Department of Conservation and Natural Resources (ADCNR) and Alabama Water Resources and Research Institute (AWRRI) (Murgulet and Tick [2006](#), [2009a,b](#)). Out of these, articles 1 and 2 make the subject of two publications in the Environmental Geology Journal (Murgulet and Tick [2007](#), [2008](#)). Article 5 will be also the subject of a technical report to AWRRI. Short versions of articles 1, 2, 3, and 4 have been presented at different international and national conferences. In addition, Articles 3, 4, and 5, have been revised and are being considered for publication in the high ranked Environmental Science & Technology journal; provided minor revisions are made.

## THE EXTENT OF SALTWATER INTRUSION IN SOUTHERN BALDWIN COUNTY, ALABAMA

### **Abstract**

Contamination of groundwater due to saltwater intrusion has become a major concern for coastal communities which rely on groundwater as their principal source of drinking water. The protection of groundwater resources from saltwater intrusion and groundwater overdraft is a critical concern in these areas as both groundwater resources and environmentally sensitive areas such as coastal wetlands and ecological coastal habitats may be at risk. A regional-scale study was conducted to assess the extent of saltwater intrusion for Baldwin County, Alabama. Groundwater wells were sampled and analyzed for salinity, chloride (Cl<sup>-</sup>), total dissolved solids (TDS), and other parameters to determine the extent of saltwater intrusion, and the location of the freshwater/saltwater interface in the region. Spatial iso-concentration maps (i.e. salinity, Cl<sup>-</sup>, and TDS) were constructed using ArcGIS software to determine the extent and severity of saltwater intrusion for the aquifers underlying Southern Baldwin County. Concentration data show relatively low salinity levels in the central and northern extent of the study area. Elevated levels of salinity, Cl<sup>-</sup>, and TDS were observed in the local Aquifers A1 and A2 along the coastal areas adjacent to the Gulf of Mexico. The study provides an initial current data set of areas impacted or most vulnerable to saltwater intrusion and provides a scientific basis for effective management of the coastal aquifers in the study region.

## **Introduction**

The coastal regions of Baldwin County are characterized by a continuously increasing economy and rate of development. Protection of groundwater resources from seawater encroachment is a real concern for coastal communities in this area due to impacts associated with increasing population, development, local industries and tourism. In addition, predictions of increasing sea level and increased frequency, and intensity of tropical storms and hurricanes in the region may exacerbate the problem over the long term.

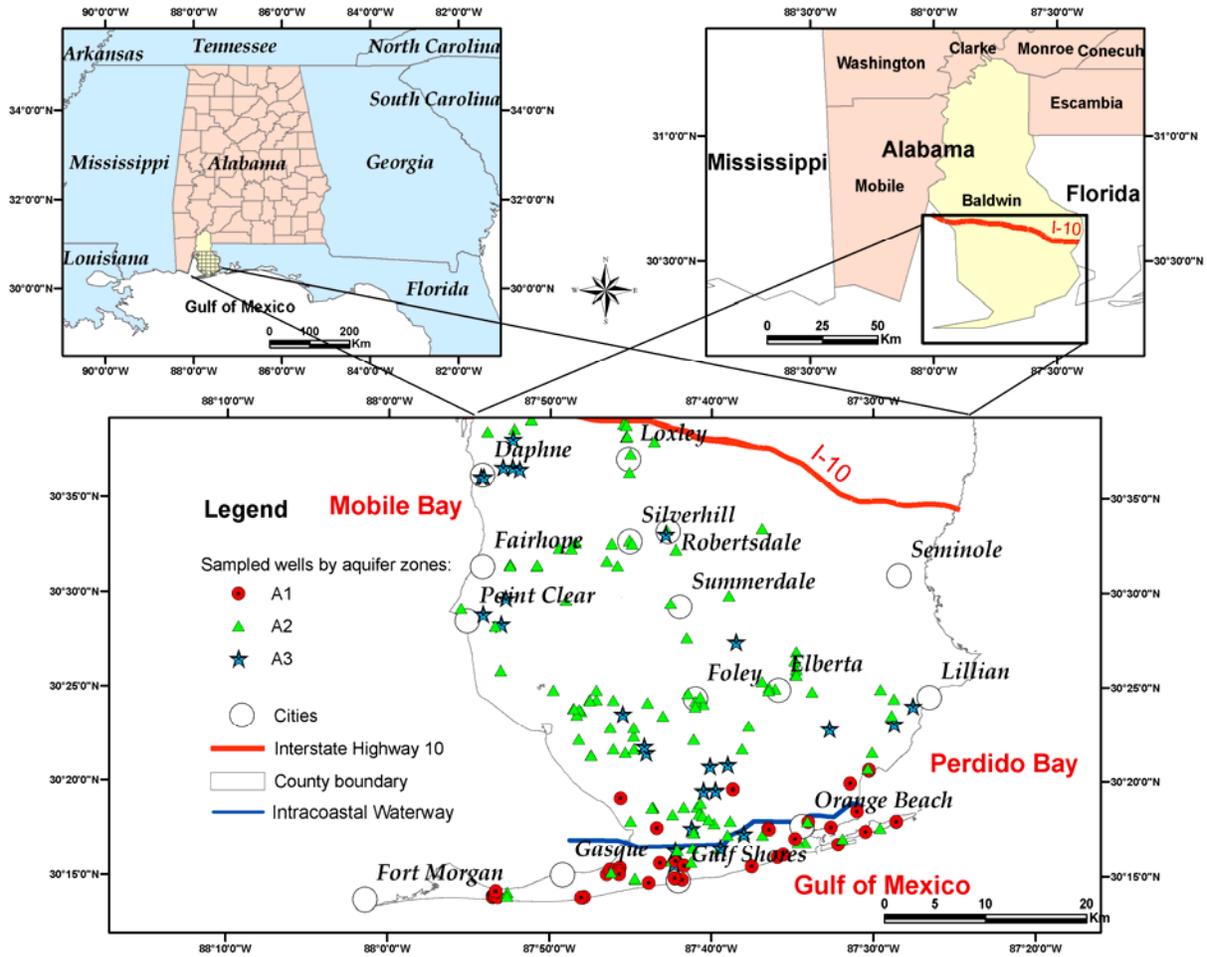
Seawater intrusion studies have been conducted on coastal aquifers in many areas adjacent to the Atlantic Ocean and the Gulf of Mexico. Although studies have been conducted in Baldwin County, regarding the hydrogeology of the area, relatively little research has been conducted on seawater intrusion and saltwater encroachment into the coastal aquifers in the region. A study by Walter and Kidd (1979) describes the groundwater chemistry and characterized the geology in detail. This study also presents management aspects for saltwater intrusion prevention, groundwater use, and the state of groundwater availability at the time. A 5 year study by Chandler et al. (1985) includes information and descriptions of the geologic and hydrogeologic environments in Southern Baldwin County as well as information about general groundwater quality. The report contains two sections on saltwater intrusion for Baldwin County revealing the freshwater/seawater interface and areas contaminated by the incursion of saltwater.

Gillett et al. (2000) published the most current study, assessing the groundwater vulnerability for the region. The purpose of this study was to determine the extent and severity of saltwater intrusion in the aquifers underlying Southern Baldwin County using the most recently collected geologic, hydrogeologic, and geochemical information. To meet these objectives, well surveys and groundwater analyses were conducted over a 1 year period (2005–2006) and

integrated with existing data attained primarily from the Alabama Department of Environmental Management (ADEM), the Geological Survey of Alabama (GSA) well records, GSA Circular 199A (Gillett et al. 2000), and GSA Bulletin 126 (Chandler et al. 1985). Site description

Location and extent of the study area Baldwin County is the largest county in Alabama, comprising an area of approximately 4,130 km<sup>2</sup>. The study area comprises approximately 1,625 km<sup>2</sup> of Southern Baldwin County and is bounded by Interstate 10 in the North, by the Gulf of Mexico in the South, and by Mobile Bay, Perdido River, and Perdido Bay in the west, Southeast and East, respectively. This region includes areas vulnerable to saltwater encroachment such as Fort Morgan Peninsula, Gulf Shores, Orange Beach, and Perdido Beach (Fig. 1). The population of Baldwin County increased significantly from 2000 with the highest rates in Fort Morgan Peninsula, Gulf Shores, Orange Beach, and Ono Island.

Baldwin County has one of the highest population increases in Alabama, second only to Shelby County. As a result of increasing population, tourism, and development, groundwater pumping in the region increased from 2.7 9 10<sup>7</sup> l/day to 1.6 9 10<sup>8</sup> l/day between 1966 and 1995 (Reed and McCain 1971; Robinson et al. 1996). Land use in Baldwin County varies considerably. The major types of land use include agriculture, recreation and tourism, seafood industries, and urbanization. Agriculture makes up approximately 40% of the land use/land cover of Southern Baldwin County (Murgulet 2006, unpublished).



**Fig. 1** Location of study area and surveyed groundwater wells (2005 – 2006)

### Hydrogeology and Groundwater Occurrence

The stratigraphy of Southern Baldwin County as well as that of coastal and offshore Alabama consists of a relatively thick Jurassic to Holocene sedimentary rocks (Chandler et al. 1985). At relatively shallow depths, interbedded sands, silts, gravels and clays comprise the middle Miocene to Holocene sedimentary rocks, which hosts the freshwater aquifer zones of Baldwin County area. The thickness of these sediments regionally decreases towards the Gulf of Mexico. The sediments are part of three widely recognized geologic units defined by Reed

(1971) as (1) the Miocene Series undifferentiated; (2) the Citronelle Formation; and (3) alluvium, low terrace, and coastal deposits. The aquifer system beneath Southern Baldwin County that serves as the source of freshwater is divided into three distinct units at the most southern portion of the study area. However, the clay aquitards, which exist in the southern of Baldwin County pinch out northward at which point the aquifer system consists of two distinct units through the central portion of the study area.

#### Aquifer Zone A1

The upper unit, known as the Beach Sand Aquifer or Aquifer Zone A1, is an unconfined aquifer consisting of white fine to coarse-grained quartzose sands, silt, and locally sandy clay with a capability of producing more than 545 m<sup>3</sup>/day (100 gallons/min) locally. Regionally, Chandler et al. (1985) estimates that Aquifer Zone A1 can yield up to 1.5 9 10<sup>5</sup> m<sup>3</sup>/day; however, only a fraction of that amount can be exploited due to the potential risks of saltwater intrusion. The Beach Sand aquifer is roughly 6–20 m thick in the study area (Chandler et al. 1985). The primary source of recharge for this aquifer comes from precipitation infiltrating the surface sands. Fresh water is lost from the zone as a result of discharging by downward infiltration to underlying zones and to the Gulf of Mexico. Larger water table fluctuations may be observed during periods of minimal precipitation or drought, wherein depth to water may be as low as 5 m below the ground surface and as little as 1.2 m below the ground surface during periods of high precipitation and recharge. Water availability for Aquifer Zone A1 is limited as a result of its vulnerability to contamination from storm and flooding events, and salt-water spray effects, particularly in low-lying areas and from overdevelopment and irrigation practices (Chandler et al. 1985).

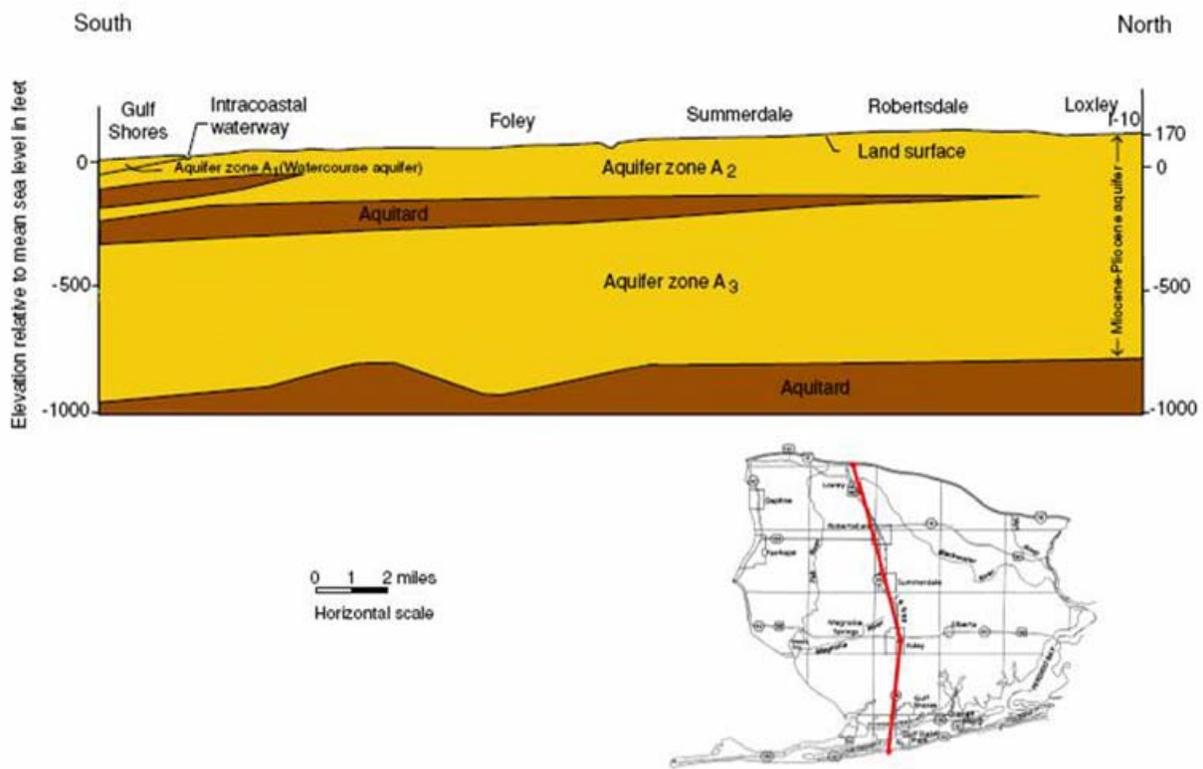
## Aquifer Zone A2

The middle unit, known as the Gulf Shores Aquifer or Aquifer Zone A2, varies locally in thickness from 60 to 75 m throughout the entire study area. This aquifer varies from confined to semi-confined to unconfined throughout extent of the study area. Along Gulf Shores and Orange Beach, the Miocene-shallow Pliocene Aquifer is confined by a marine clay layer, which completely ends northward of the study area (Chandler et al. 1985). In the southern extent of the study area, the aquifer is approximately 20–30 m thick, and it is hydraulically separate from the Beach Sands water-table aquifer by a 10-15 m thick marine clay unit (Kidd 1988). The aquifer is extensively developed as a source of fresh water for municipal, industrial, private, and irrigation wells. Production rates from this unit range from 545 to 5,450 m<sup>3</sup>/day (100–1,000 gallons/min). Recharge to this aquifer zone primarily occurs from rainfall where the unit crops out to the North under unconfined conditions (Chandler et al. 1985). Aquifer A2 is vulnerable to surface contamination towards the North as it becomes unconfined.

## Aquifer Zone A3

The lower unit is known as the Deep Miocene Aquifer or Aquifer Zone A3. This hydrologic unit is similar to the Gulf Shores Aquifer (A2) in terms of lithology, with the exception that the sand and clay layers are more defined. The aquifer extends from the upper confining unit that underlies Aquifer Zone A2 to the top of the Pensacola Clay (200 m to more than 300 m below sea level). The aquifer ranges in thickness from roughly 90 to 175 m, and has a capacity of producing fresh water of more than 8,200 m<sup>3</sup>/day (1,500 gallons/min). Groundwater is typically present under confined or artesian conditions. The majority of public water supply wells are completed within this aquifer due to its limited exposure to sources of surface contamination. However, it has been mentioned in previous studies (Chandler et al. 1985; Gillett

et al. 2000) that the unit is with salt water in the area of Fort Morgan Peninsula. The aquifer receives much of its recharge from precipitation and resulting infiltration, where the confining unit thins out and the aquifer unit crops out into the northern part of the study area. A cross section of the study area illustrating hydrostratigraphic units is shown in Fig. 2.



**Fig. 2** Hydrogeologic cross section of Southern Baldwin County, Alabama (modified from Gillett et al., 2000)

### Methodology

To meet the objectives of this paper, the first attempt was to link the hydrogeologic system and groundwater geochemical data of Southern Baldwin County to spatial statistics and map modeling. Such integration allows, for example, meaningful identification of the seawater

contaminated regions. For this purpose, geologic and hydrogeologic information, and groundwater quality parameters including salinity, Cl<sup>-</sup>, and TDS concentrations were collected and compiled to generate spatial distribution and contamination maps. For the purposes of this study and consistency with current definitions, “freshwater” is considered to be water comprising concentrations no more than 500, 250, and 500 mg/L for salinity, Cl<sup>-</sup>, and TDS, respectively (MCLs “maximum contaminant levels” are reported by USEPA 1992). Once these limits are exceeded, the water is no longer potable for drinking water purposes and additional water treatment is needed or well abandonment or discontinued operation is required. The relationships between the three parameters were examined as a means of assuring consistency between samples and verification of the saltwater source (i.e., intrusion from the Gulf of Mexico).

Advanced spatial analysis techniques were applied to raster data representing a set of constraints that may be encountered in a contamination project. Digital maps have been produced and used to construct a spatial database for the study area. Results obtained from this methodology have been incorporated with data collected for this project and used to create the final contamination digital maps.

#### Data Collection

An extensive collection of geologic, hydrogeologic, and water chemistry data was conducted for Southern Baldwin during a 1 year period between 2005 and 2006. Groundwater samples were collected from public supply wells, private supply wells, and industrial and irrigation groundwater wells during numerous field visits to the region. The spatial locations (i.e., longitude, latitude) of surveyed wells were recorded using GPS (Fig. 1). Surveyed wells were monitored for water level (hydraulic head) and well depth.

In addition, a wealth of information and data was collected and gleaned from GSA, ADEM, local water utilities, golf courses, agricultural farms, and numerous other businesses and private well owners across Southern Baldwin County (Fig. 2).

### Sample Analysis

Groundwater samples were analyzed for salinity,  $\text{Cl}^-$ , TDS, conductivity, resistivity, oxidation–reduction potential (ORP), pH, and temperature. All samples represent raw water samples collected from taps at the wellhead (after purging). Over 400 analysis measurements were determined for approximately 200 sampled wells during this 1 year period. As a means to assure consistency and confidence in the results of the sample analyses,  $\text{Cl}^-$  concentrations were independently measured using two different methods: a specific combination electrode (Denver Instruments) and an ion chromatograph (Dionex Instruments). Groundwater chemical field parameters including conductivity, resistivity, ORP, pH, and temperature were measured using a portable field multi-meter (Ultrameter II 6P, Myron L Company). Salinity was measured using a portable field salinity meter (EC400, ExTech Instruments). Samples were analyzed for  $\text{Cl}^-$  at laboratory facilities housed within the Department of Geological Sciences at the University of Alabama. Chloride specific electrode analyses were conducted in the Contaminant Hydrogeology Laboratory and ion chromatography (IC) analyses were conducted in the Geochemical Analytical Facility. For specific electrode analyses, samples were removed from the refrigerator, allowed to equilibrate to room temperature, and analyzed using a seven-point standard curve ranging from 1 to 1,000 mg/L. The samples were analyzed using a specific chloride electrode (Model # 300742.1, Denver Instruments Co.) coupled to a multi-meter (Model 250, Denver Instrument Co.). Samples were diluted as necessary to remain within the linear range of the instrument. The method detection limit for this method was approximately 1 mg/L.

For IC analyses, concentrations of chloride were determined with a Dionex High Performance Ion Chromatograph (Model DX600, Dionex Corp., Sunnyvale, CA, USA) equipped with an autosampler, an anion-exchange column (7 mm; 4 9 250 mm; Dionex AS14A), and a conductivity detector (Dionex CD25). The lower detection limit of the method was approximately 0.01 mg/L.

### Geographic Information System (GIS)

All data relevant to the saltwater contamination of groundwater were collected, including for instance, but not exclusively, topography, geology, land-use/land-cover, hydrology, hydrogeology, and rainfall amounts, as well as existing aerial photographs and satellite imagery. ArcGIS was used to compile the geospatial data, to record and map well locations, well depths, hydrogeological information, and concentration data collected from fieldwork and allowed for the generation of iso-concentration maps, groundwater elevation maps, and groundwater flow maps. The spatial database for the project was built in the raster and vector formats inside the GIS. The output maps elaborated for this study are shown in Figs. 3, 4, and 5. Spatial features identified as the most sensitive (e.g., elevation, and geochemical and geological data) to this saltwater intrusion impact study have been gathered by categories and subsequently integrated into a raster map, which was created for each constraint. The grid layer for depth to water and saturated thickness of each aquifer zone was generated by computer subtraction of water-level elevation data sets from land surface elevation. Land surface elevations were derived from a Digital Elevation Model (DEM) for the Southern Baldwin County area. The water-level elevation data sets were obtained from field measurements and from the groundwater well records available at GSA and ADEM. Iso-concentration and groundwater elevation maps were prepared to determine areas vulnerable to saltwater intrusion and the extent of saltwater intrusion

for each of the developed aquifer zones. Specifically, salinity,  $\text{Cl}^-$ , and TDS concentration and groundwater level data were interpolated to construct the iso-concentration and groundwater elevation (potentiometric surface) maps. The Geostatistical Analyst extension was used to interpolate the data. For more confidence, the output maps were compared with output maps developed from interpolation of same data using Surfer software package (Golden Software, Inc.) and compared with the actual concentrations and water levels.

The kriging interpolation method proved to be the most effective at simulating iso-concentration and potentiometric surface contours when compared to the observed data distribution. The output concentration grid layers for each of the three parameters (salinity,  $\text{Cl}^-$ , and TDS) were reclassified using the binary masking method. The aim of this reclassification was to develop the final concentration maps that delineate only those sections affected by saltwater intrusion as indicated by concentrations of salinity,  $\text{Cl}^-$ , and TDS above regulatory MCLs. The reclassification process involved development of a new raster layer by changing the attribute values of the cells of the input layers. Through this process, critical areas such as those that exceed  $\text{Cl}^-$  concentrations of 250 mg/L, salinity concentrations of 500 mg/L and TDS concentrations of 500 mg/L were identified. A new grid based on the new criteria was developed for each aquifer using the Spatial Analyst extension, raster calculator tool. Groundwater elevation maps were constructed to determine local and regional groundwater flow directions. Groundwater elevation contours (i.e., potentiometric surface contours) are shown in Figs. 3d, 4d, and 5d for Aquifer Zones A1, A2, and A3, respectively.

## **Results**

An abundance of data (2005–2006) were collected and compiled into a user friendly GIS database allowing for useful graphical visualizations (i.e., table and figures), data interpretation,

data analyses, and current assessments of groundwater quality (i.e., saltwater intrusion) and availability (i.e., groundwater flow) for the region. Data from approximately 200 wells throughout Baldwin County were included in the database and analyzed in order to determine the extent of saltwater intrusion for the study area. Integration of hydrogeologic data and groundwater geochemical parameters (i.e., salinity,  $\text{Cl}^-$ , TDS, etc.) with spatial location and map modeling allowed for robust identification of the seawater contaminated regions. Examination of the salinity,  $\text{Cl}^-$ , and TDS parameters revealed the Gulf of Mexico to be the source of saltwater intrusion.

Water level measurements were recorded to assess both local and regional groundwater flow and gradients for each aquifer zone. The encroachment of saltwater into coastal aquifers can be recognized by elevated salinity,  $\text{Cl}^-$ , and TDS concentrations. In addition, elevated measurements of resistivity and specific conductance were used to help in evaluating areas affected by saltwater intrusion.

#### Regional and Local Groundwater Flow

Groundwater elevation maps constructed from the collected water level data provided the current state of regional and local groundwater flow for the study (Figs. 3d, 4d, and 5d).

Groundwater flow directions were determined to be predominantly South, South-Southwest, and South-Southeast. For Aquifer Zone A1, groundwater flow trended South and South-Southwest with hydraulic gradients of approximately 0.001 and 0.0006, respectively and relatively steeper hydraulic gradients observed in the South-Southwest direction.

For Aquifer Zone A2, groundwater flow direction trended to East, Southeast, South, and Southwest with hydraulic gradients of approximately 0.0006, 0.0013, 0.0013, and 0.0016, respectively and relatively steeper hydraulic gradients observed in the South, Southwest and

Southeast directions. For Aquifer Zone A3, groundwater flow direction trended to Southeast, South-Southeast, and Southwest with hydraulic gradients of approximately 0.001, 0.00083, and 0.00016, respectively and relatively steeper hydraulic gradients observed in the Southeast direction.

### Groundwater Chemistry and Availability

The availability of groundwater for public and private use is primarily dependent upon the volume capacities of the aquifer itself. However, in regions that are vulnerable to contamination, such as coastal aquifers experiencing saltwater intrusion, large volumes of water can be rendered unsuitable for use due to degraded water quality (i.e., high salinity, TDS,  $\text{Cl}^-$ , etc.). Minimum, maximum, and average values of groundwater chemical concentrations for each respective hydrogeologic unit are included in Table 1. Iso-concentration maps are presented, displaying the zones impacted by saltwater intrusion (Figs. 3, 4, 5). It is important to recognize that the iso-concentration maps utilize interpolation schemes (i.e., kriging) based on available data. Due to the fact that some areas within the region lack any well data, concentrations of water quality parameters (i.e., salinity,  $\text{Cl}^-$ , and TDS) may not be revealed by the figures. Hence, it should be clear that these apparently “non-impacted” regions may in reality possess elevated levels of salinity,  $\text{Cl}^-$ , and TDS. Along the narrow coastal zones of the study area, elevated concentrations of salinity,  $\text{Cl}^-$ , and TDS were observed for both Aquifer Zones A1 and A2. Groundwater samples from Aquifer Zone A1 exhibited elevated concentrations of salinity,  $\text{Cl}^-$ , and TDS in the close coastal proximity of Gulf Shores, Orange Beach, Ono Island, and Laguna Keys (Fig. 3a, b, c).

The average salinity concentration for Aquifer Zone A1 was determined to be 1,153.9 ppm (mg/L) with a maximum concentration of 18,000 ppm (mg/L) in close proximity to the

coastline. The average chloride concentration for Aquifer Zone A1 was determined to be 486.2 mg/L with a maximum concentration of 7,758.3 mg/L in close proximity to the coastline of Gulf Shores. Similarly, along the southern coastal boundary of Baldwin County, the groundwater samples in Aquifer Zone A1 revealed relatively high TDS concentrations. The average TDS concentration for Aquifer Zone A1 was determined to be 1,359.3 ppm (mg/L) with a maximum concentration of 14,590 ppm (mg/L).

Aquifer Zone A2, a principal water bearing aquifer for Baldwin County, has been extensively developed for domestic, agricultural, municipal, and industrial uses. Groundwater in Aquifer A2, near the coastal margin, was determined to possess lower water quality with relatively high salinity, Cl<sup>-</sup>, and TDS concentrations (Fig. 4a, b, c). The average salinity concentration for Aquifer Zone A2 was determined to be 96.8 ppm (mg/L) with a maximum concentration of 2,590 ppm (mg/L) just North of Highway 182 in Gulf Shores. The average chloride concentration for Aquifer A2 was determined to be 28.2 mg/L with a maximum concentration of 1,460.4 mg/L North of Romar House in Gulf Shores. The average TDS concentration for Aquifer Zone A2 was determined to be 146.8 ppm (mg/L) with a maximum concentration of 3,610 ppm (mg/L) at the same location in Gulf Shores.

Table 1. Results of water analyses by hydrogeologic unit

Water analysis parameter (unit)	Limits for fresh water (EPA, 1986)		Hydrogeologic unit								
	Human consumption	Irrigation	Aquifer Zone A1			Aquifer Zone A2			Aquifer Zone A3		
			Low	High	Average	Low	High	Average	Low	High	Average
Chloride (mg/L)	250	250	6.9	7758.3	486.2	1.8	1460.4	28.2	2.9	18.2	13.6
Salinity (mg/L)	500	-----	32.3	18,000.0	1153.3	13.2	2590.0	96.8	12.6	136.0	39.5
TDS (Total Dissolved Solids (mg/L))	500	500-1,000 TDS (dependent upon crop sensitivity)	45.6	14590.0	1359.3	18.5	3610.0	146.8	14.8	190.0	51.4
pH	6.5-8.5	-----	4.7	7.6	6.5	4.5	8.0	5.1	4.6	8.0	5.8
Specific conductance (µS)	-----	-----	64.9	25700.0	2019.7	26.6	5170.0	181.2	53.0	151.9	81.6
Resistivity (kΩ)	-----	-----	11.7	16.4	13.4	10.1	38.4	18.0	18.9	38.4	27.8

Chloride = chloride concentration in water

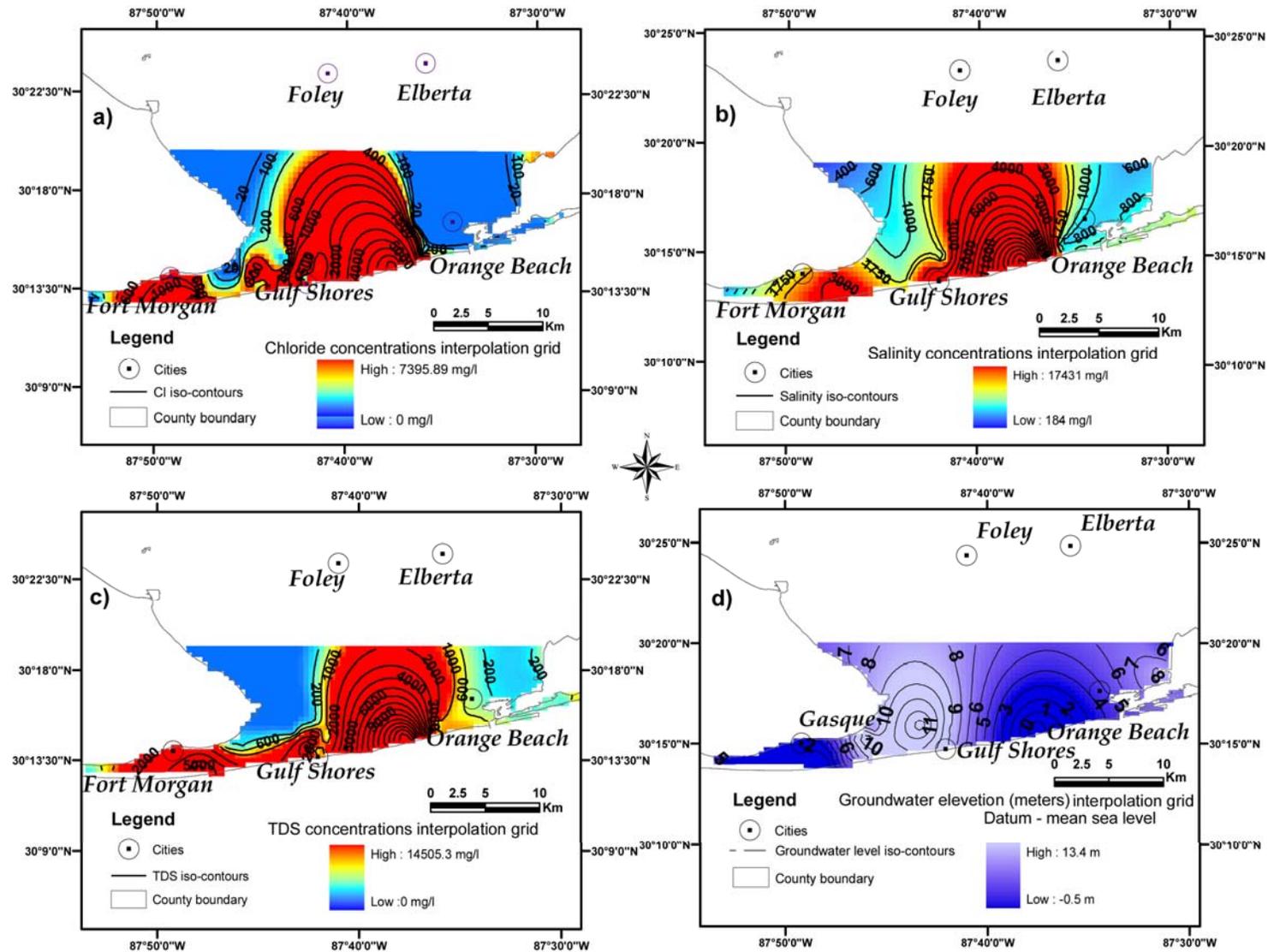
Salinity = the concentration of mineral salts and solids dissolved in water.

TDS = Total Dissolved Solids is an expression for the combined content of all inorganic and organic substances contained in a liquid.

COND = electrical conductivity

pH = a measure on a scale from 0 to 14 of the acidity or alkalinity of a solution (where 7 is neutral, greater than 7 is more basic, and less than 7 is more acidic)

Resistivity = a measure of how strongly water opposes the flow of electric current (pure water is not considerably conductive).

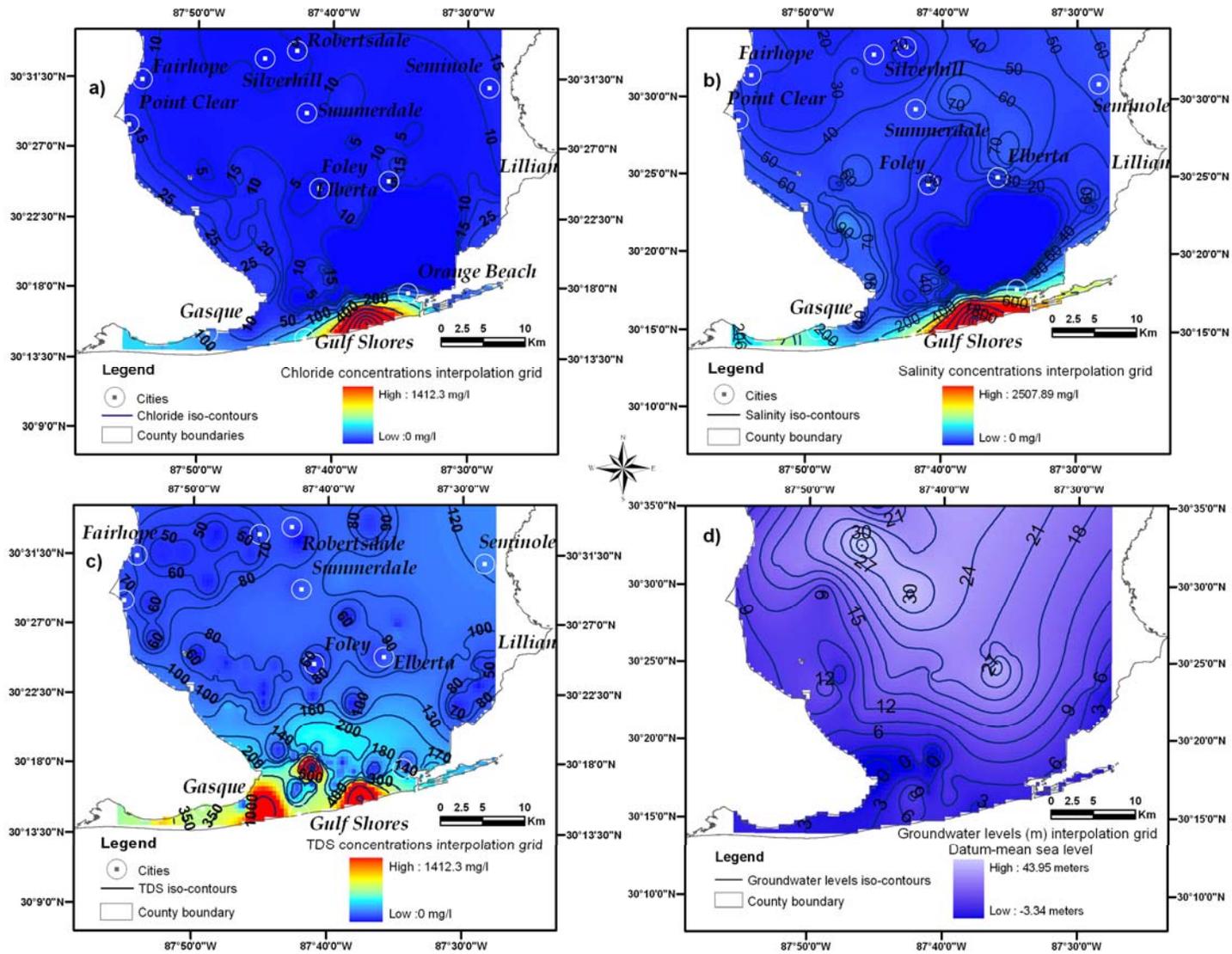


**Fig. 3** Aquifer Zone A1 a) Chloride concentration map; b) Salinity concentration map; c) TDS concentration map; d) Groundwater potentiometric surface and general flow directions. Concentrations are in mg/L; contour lines are labeled correspondingly

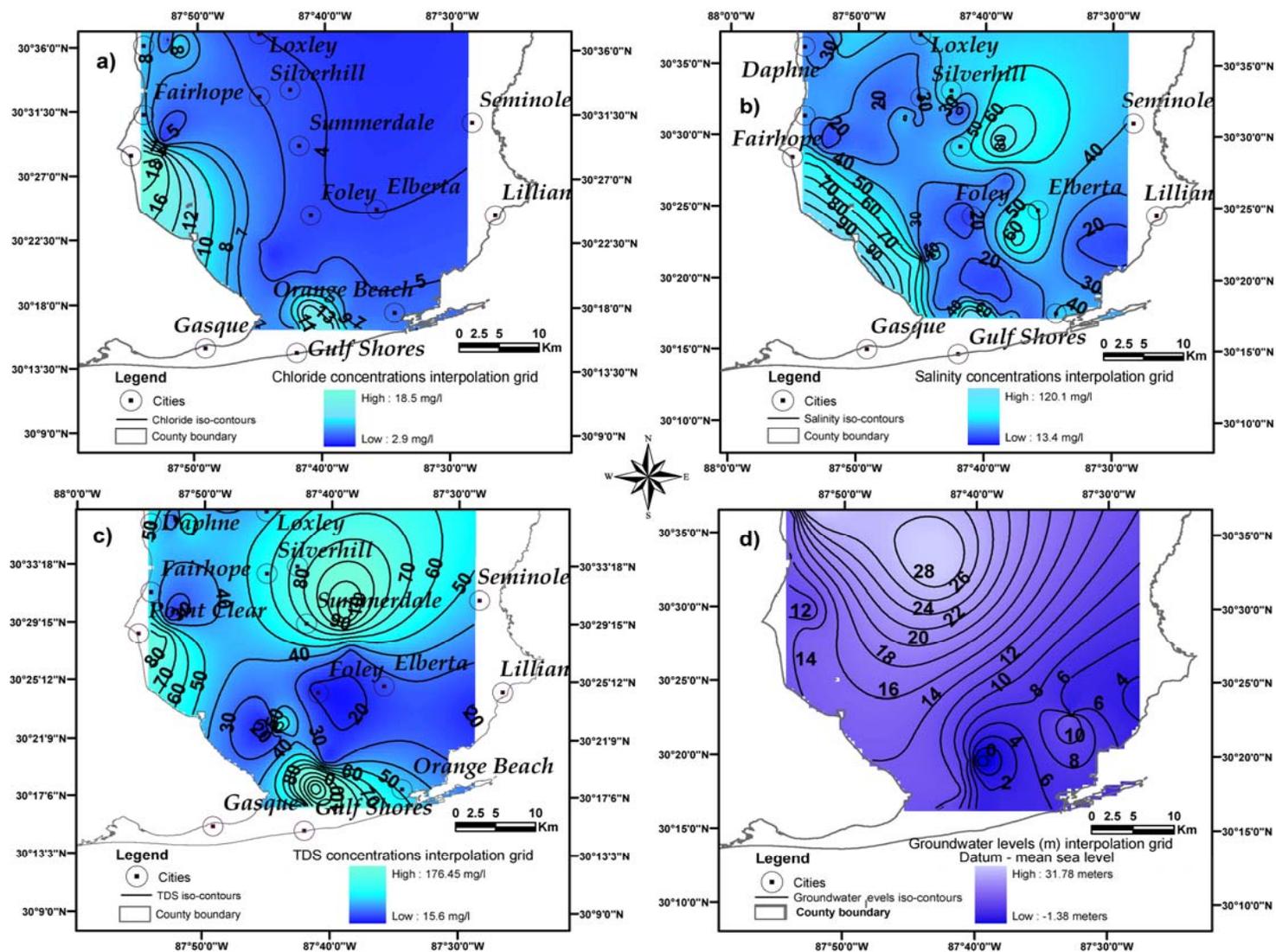
Aquifer Zone A3 has been extensively developed for municipal uses. The majority of the public water supply wells are completed within this aquifer unit due to its limited vulnerability to sources of surface contamination. However, as Chandler et al. (1985) points out, it is important to note that this aquifer can be affected by saltwater contamination due to saltwater intrusion, as evidenced by elevated salinity levels in the lower portion of the aquifer and extending a considerable distance inland (Chandler et al. 1985, Fig. 2). As part of this current study, groundwater samples obtained from wells completed in Aquifer Zone A3 exhibited low concentrations of salinity,  $\text{Cl}^-$ , and TDS (Fig. 5a, b, c).

The average salinity concentration for Aquifer Zone A3 was determined to be 39.5 ppm (mg/L) with a maximum concentration of 136 ppm (mg/L) North of the Intracoastal Waterway in Gulf Shores. The average chloride concentration for Aquifer Zone A3 was determined to be 13.6 mg/L with a maximum concentration of 18.2 mg/L at the same location in Gulf Shores. The average TDS concentration for Aquifer Zone A3 was determined to be 51.4 ppm (mg/L) with a maximum concentration of 190 ppm (mg/L) North of the Intracoastal Waterway in Gulf Shores, at the same location where the highest chloride and salinity concentrations were observed.

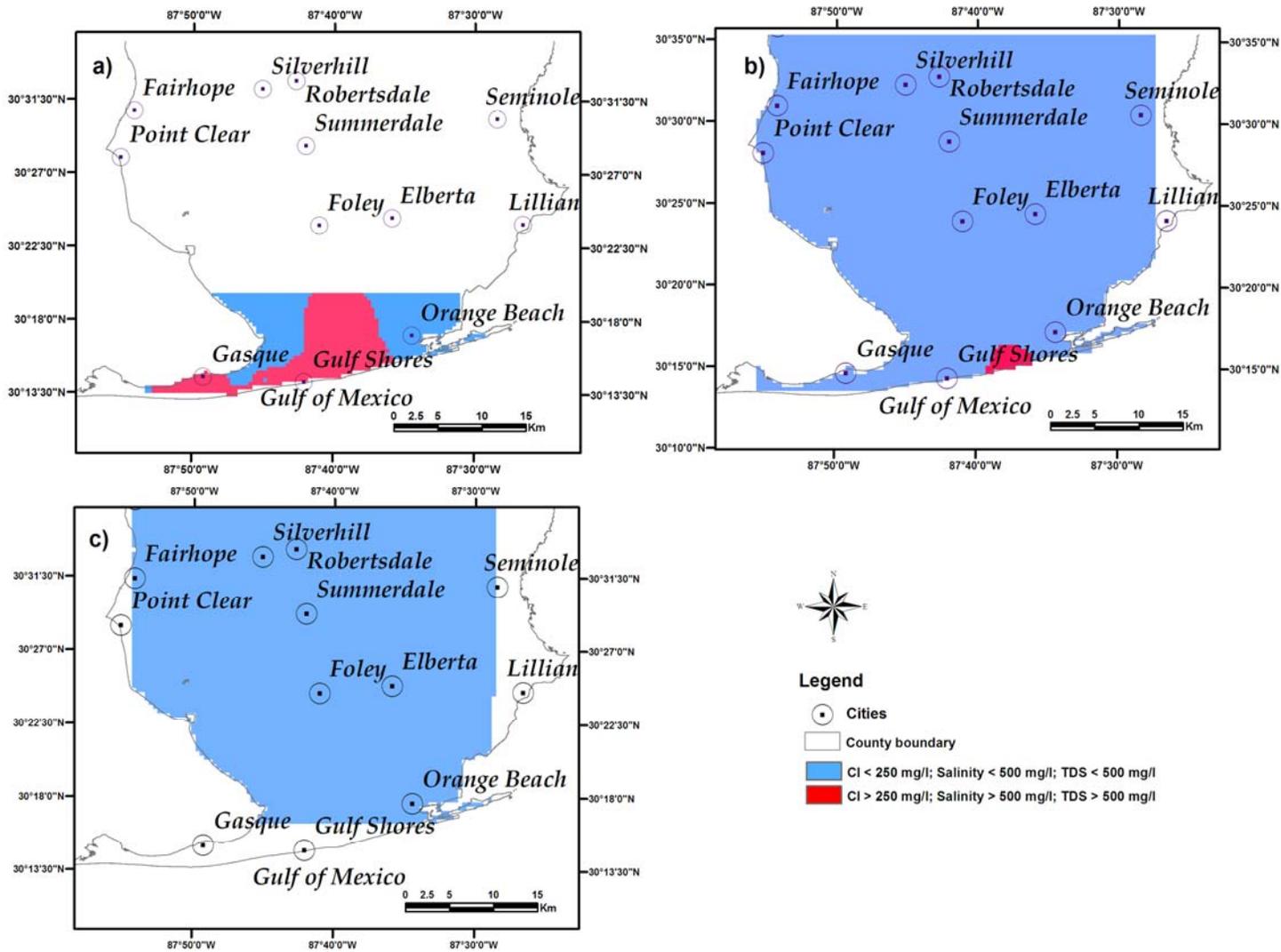
Obtaining data from this Aquifer unit (A3) proved to be difficult, especially along the coastal zones of the study area, as wells that were established within this aquifer, in close proximity to the coastline, have for the most part been shut down, abandoned, or have limited access (Blakeney Gillett, GSA, personal communication, 2006). This may suggest that these wells are either established in a relatively shallow portion of the Aquifer Zone A3 or that the aquifer has not been infiltrated with saline water in that region.



**Fig. 4** Aquifer Zone A2 a) Chloride concentration map; b) Salinity concentration map; c) TDS concentration map; d) Groundwater potentiometric surface. Concentrations are in mg/L; contour lines are labeled correspondingly



**Fig. 5** Aquifer Zone A3 a) Chloride concentration map; b) Salinity concentration map; c) TDS concentration map; d) Groundwater potentiometric surface and general flow directions. Concentrations are in mg/L; contour lines are labeled correspondingly



**Fig. 6** Contamination maps by aquifer zones: a) Aquifer Zone A1; b) Aquifer Zone A2; c) Aquifer Zone A3

## Discussion

The groundwater system of Southern Baldwin County comprises of three hydraulically distinct aquifers that will likely provide ample supply if properly managed. However, saline water intrusion from aquifer overproduction or storm events is a potential problem for the coastal region of the study area. The results of this study indicate that saltwater intrusion may have occurred in Aquifer A1, especially in regions relatively close to the Gulf of Mexico. The elevated salinity,  $\text{Cl}^-$ , and TDS concentrations may be the result of a combination of both saltwater intrusion and surface contamination. Aquifer Zone A1 is vulnerable to saltwater intrusion, in the close proximity of the Gulf of Mexico, from storm events due to seawater surface infiltration. Another source of contamination of Aquifer A1 may be due to the direct infiltration from the Intracoastal Waterway, which crosses the southern part of the study area from East to West (Figs. 1, 2) and from saltwater ponds located along the Intracoastal Waterway. Aquifer Zone A2 is vulnerable to saltwater intrusion, particularly in areas where wells are in close proximity to the Gulf of Mexico. The results of this study indicate that saltwater intrusion has occurred in Aquifer A2, specifically in close proximity to the Gulf of Mexico. The results are confirmed by field data that exhibited elevated levels of salinity,  $\text{Cl}^-$ , and TDS for these noted areas.

Saltwater contamination of Aquifer Zone A2 might be the result of aquifer overdevelopment and infiltration from Aquifer A1. Groundwater samples and iso concentration maps revealed that Aquifer Zone A3 did not exhibit significant degradation of water quality due to saltwater intrusion. As it might be expected, the groundwater concentration data suggest that Aquifer Zone A3 is less vulnerable to saltwater intrusion. However, this does not mean that saltwater intrusion has not occurred or exists within this aquifer zone. It may be that the

relatively low number of wells and depth of these wells were too shallow to capture high concentration regions of salinity,  $\text{Cl}^-$ , and TDS within this aquifer (A3). The potential extent of saltwater intrusion for the study area can be observed from the groundwater contamination (iso-concentration) maps (Fig. 6). These maps reveal the regions that exceed regulatory limits for salinity,  $\text{Cl}^-$ , and TDS.

To define the extent of saltwater intrusion along the entire coastal region, more wells need to be constructed in areas that lack data. This will improve the current iso-concentration maps; however, the addition of wells to these sparsely populated areas may be too costly and/or not feasible to implement. Further monitoring of the salinity and chloride levels in this aquifer, especially near the coastal margin of the study area, is necessary to evaluate the evolution of the saltwater and water quality conditions over time. Proper well placement and regulation in terms of groundwater withdrawal is important to prevent Aquifer Zones A2 and A3 from experiencing such problematic conditions associated with saltwater intrusion.

ArcGIS proved to be a valuable tool used to determine the spatial extent of saltwater intrusion. ArcGIS was effectively used to produce groundwater elevation (potentiometric surface) maps and assess groundwater flow conditions for the study area. The method used to determine regions affected by saltwater intrusion includes those areas that revealed concentrations exceeding the maximum contaminant level (MCL) for salinity,  $\text{Cl}^-$ , and TDS (Table 1; USEPA 1992). In addition, the use of GIS makes it possible to view the data in a viable format for those who make regulatory decisions, whereas such data in the past has been much less accessible. Furthermore, the use of these tools provides an opportunity to assemble, standardize, and analyze scientific data that comes from a variety of sources, making it available to others who may be able to continue with further research studies.

## **Acknowledgments**

Funding for this project was provided in part by Award Number NA#04NOS4190029 through the Coastal Zone Management Act of 1972 (as amended), administered by the Office of Ocean and Coastal Resource Management, National Oceanic and Atmospheric Administration and in conjunction with the Alabama Department of Conservation and Natural Resources (ADCNR), State Lands Division. We would like to extend our gratitude to Mr. Carl Ferraro from ADCNR who played a primary role in initiating the funds for this project and providing invaluable assistance along the way. We would also like to thank Dr. Enid Probst from (ADEM), the Geological Survey of Alabama, and Weeks Bay Reserve for providing assistance and guidance along the process. We would especially like to thank the people of Baldwin County who generously provided access to their wells.

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## ASSESSING THE EXTENT AND SOURCES OF NITRATE CONTAMINATION IN THE AQUIFER SYSTEM OF SOUTHERN BALDWIN COUNTY, ALABAMA

### **Abstract**

A regional-scale groundwater study was conducted over a 2-year period to assess the extent of nitrate contamination and source identification for Southern Baldwin County, AL. Groundwater wells were sampled and analyzed for nitrate and a host of other geochemical parameters which revealed that extensive areas within Aquifer Zone A2 exhibited nitrate concentrations exceeding regulatory limits. Spatial iso-concentration maps of nitrate were constructed using ArcGIS software to determine the extent and severity of contamination for the aquifers underlying Southern Baldwin County with the primary interest focused on the heavily utilized Aquifer Zone A2. Nitrate levels in the central and northeastern portion of the study area were most extensive with maximum concentrations of 63 mg/L likely resulting from agricultural inputs. Several other small regions throughout the study area exhibited elevated levels of nitrate and chloride as high as 112 and 51.1 mg/L, respectively, and sources likely vary (i.e., residential septic systems, animal waste to agriculture). With the exception of a few groundwater samples, there was no obvious correlative relationship between chloride and nitrate concentration for data collected during the 2-year period. Collectively, a general inverse relationship between nitrate concentrations and well depth was observed for the aquifer system under investigation. The study provides an initial current data set of areas impacted or most vulnerable to nitrate contamination and initial assessment of likely sources of nitrate in the region.

## Introduction

The contamination of groundwater from nitrate and nutrients is a major problem throughout the world. These related problems are often the result of anthropogenic activities, lack of management, and overdevelopment of water resources. Recently, a high level of interest has been generated in thoroughly understanding rates of exchange and loading of nitrates/nutrients between groundwater and surface water systems. Therefore, it is essential to conduct detailed assessments of the spatial and temporal distributions of nitrate contamination in these systems. The assessments made from land-use/land-cover analysis are critical for identifying the location and origin of these nitrate sources to groundwater and surface water so that appropriate management and/or remediation strategies can be implemented proactively or in a timely manner.

Groundwater is recognized as a potential source of nutrients and other contaminants that affect the ecology of estuaries and coastal fresh water bodies (USEPA 1996). Nitrogen, phosphorous, and suspended solids are just a few of the contaminants that can contribute to the deterioration of water quality in agriculturally dominated and rural areas with heavy fertilizer application, and residential areas with improperly functioning septic systems. The nitrate problem is most evident in the mobile form of  $\text{NO}_3^-$  and it is known to cause health problems in humans (Rajagopal and Tobin 1989) and contribute to the eutrophication of surface waters (Cooper 1993). Currently, there is a lack of information and understanding of  $\text{NO}_3^-$  input and its effect on the quality of water resources and ecosystem health within these highly sensitive areas of Alabama (i.e., coastal estuaries/wetlands, and riparian and lake systems). Some of the major concerns of  $\text{NO}_3^-$  contamination/loading to both these groundwater and surface water systems include health risks to humans through drinking water (i.e., methemoglobinemia and potential

carcinogenic effects), and degradation of the local ecosystems (i.e., excessive plant and algal growth). A large majority of nitrate sources are anthropogenic of origin and are commonly confined to the same watershed and groundwater basin. In aquifer systems more prone to nitrate contamination, surficial aquifers are more likely to be contaminated and at a greater extent compared to deeper, confined or unconfined aquifers. Inverse relationships between nitrate concentration and aquifer depth have been noticed in previous studies (Spalding and Exner 1993; Clawges and Vowinkel 1996; Kehew et al. 1996; Ray and Schock 1996). The contaminants coming from these various sources can be transported to surface waters by surface runoff and groundwater discharge. Several studies indicate that rural land uses, especially agricultural practices, can cause nitrate contamination of underlying groundwater (Vowinkel and Tapper 1995; Bouwer 1978; Driscoll 1986). In addition, regions experiencing significant population growth may be substantially contributing to the groundwater nitrate contamination (Bouwer 1978; Driscoll 1986; NRC 1993). In some instances it has been observed that elevated nitrate concentrations are accompanied by increased chloride concentrations. In places where fertilizers are applied to the land surface there is an increased potential for groundwater contamination due to the direct downward infiltration of nitrate to the aquifer system. These sources, however, do not necessarily coincide with increased concentrations of chloride in groundwater. Alternative sources such as sewer breakthrough and animal waste can cause a significant increase of both nitrate and chloride concentrations (Canter and Knox 1985; Alhajjar et al. 1990; Robertson et al. 1991; Kehew et al. 1996; Hudak and Blanchard 1997). The concentrations for septic tank effluent typically varies between 77 and 111 mg/L total nitrogen and 37 and 101 mg/L chloride (Canter and Knox 1985).

The purpose of this study was to determine the extent and severity of nitrate contamination and assess changes in nitrate levels over a 2-year period in the aquifers underlying Southern Baldwin County. In addition, this study aims to identify the potential source zones and the origin of these nitrate sources contributing to groundwater pollution. To meet these objectives, well surveys and groundwater analyses were conducted over a 2-year period (2006 and 2007) and integrated with existing data obtained primarily from the Alabama Department of Environmental Management (ADEM), and the Geological Survey of Alabama (GSA) well records.

### **Background**

In recent years, Baldwin County has experienced some of the most rapid growth in public and private sectors, ranking second among all counties within the state of Alabama. As a result, observed decreasing quality of groundwater and surface water due to extensive agricultural practices, and urban and residential expansion has become an increasing concern for the region. Groundwater and surface water resources in Southern Baldwin County, AL, are vital to support the rapidly growing population of the area, the emerging economy within the region, and to ensure that environmentally-sensitive ecosystems such as coastal estuaries and wetlands are preserved in the region. The regional population, tourism, and industry are dependent upon the quality and quantity of the water resources and health of the ecosystems within the region.

In Southern Baldwin County, agriculture and residential application of fertilizers, sewage breakthrough, transport via runoff and precipitation, and land application of animal waste are some of the major sources that may contribute to nitrate/nutrient contamination of groundwater and surface water. Nitrate contamination may be a potential problem in some of the aquifers of Baldwin County as nitrate levels in wells have been observed to exceed regulatory drinking

water standards (45 mg/L as nitrate; or equivalently 10 mg/L nitrate as nitrogen). Not only is this a concern for human health, but groundwater discharge and surface runoff of elevated nitrate levels to coastal surface waters and/or streams can have harmful effects on the ecological health of coastal wetlands, estuaries, and riparian zones. Excess nitrate (i.e., nutrient) loading can cause processes such as eutrophication which can adversely impact the ecology of these systems. The existence of the saltwater intrusion problem in the coastal areas of Baldwin County may further enhance the  $\text{NO}_3^-$  flux associated with ion exchange and other interdependent reactions (Moore 1999; Krest et al. 2000). Hence, contamination of the aquifer system from elevated concentrations of nitrate may pose real concerns due to increased anthropogenic activity. Therefore, it is imperative to identify sources of nitrate contamination/loading and to determine the status of groundwater quality for this area allowing for better source control strategies and management. The results of this research will be critical for developing cost-effective aquifer management plans to ensure sustainable freshwater supplies and preserve the health of the regional ecosystems (i.e., wetland/estuaries, riparian zones, and lakes) in the study area. This is the first known study to assess the extent and severity of nitrate contamination in the aquifer system underlying Southern Baldwin County, AL.

### **Previous Studies**

Although studies have been conducted in Baldwin County pertaining to the hydrogeology of the area, relatively little research has been conducted on defining the extent and identifying potential sources of nitrate contamination within the aquifers of Southern Baldwin County, AL. Relevant hydrogeologic and water resource studies for the study area include the GSA (Geological Survey of Alabama) Circular 199A (Gillett et al. 2000), the GSA Bulletin 126 (Chandler et al. 1985), and a GSA Open-file Report (Walter and Kidd 1979; Kidd 1988). The

most current studies of this region were conducted by Liu et al. (2007) and Murgulet and Tick (2007). Liu et al. (2007) investigated the current state of groundwater withdrawal from Fort Morgan Peninsula (Southern Baldwin County, Alabama) providing a capture zone analysis for the area. Their results indicate that under current groundwater extraction rates, the Fort Morgan Peninsula region exhibited extensive cones of depression making the aquifers in this area highly susceptible and vulnerable to saltwater intrusion. Murgulet and Tick (2007) conducted an extensive regional study evaluating the current extent of saltwater intrusion in Southern Baldwin County, AL. The results from this study indicated that groundwater quality in Southern Baldwin County is being degraded in close proximity of the coast, due to elevated chloride and salinity concentrations.

A previous study in Southern Baldwin County, AL, was conducted by Dowling et al. (2004), which attempted to quantify nitrate flux to the Gulf of Mexico using indirect proxies to estimate recharge and discharge through the aquifer system. This study, however, did not directly assess or quantify nitrate concentrations, but rather quantified groundwater discharge rates to predict nutrient loading to the Gulf of Mexico. These previous studies do not directly measure the extent or concentrations of nitrate within the local and regional aquifer systems, and therefore, no attempts have been made to identify potential sources or origins of nitrate within Southern Baldwin County, AL.

## **Site Description**

### **Location and Extent of the Study Area**

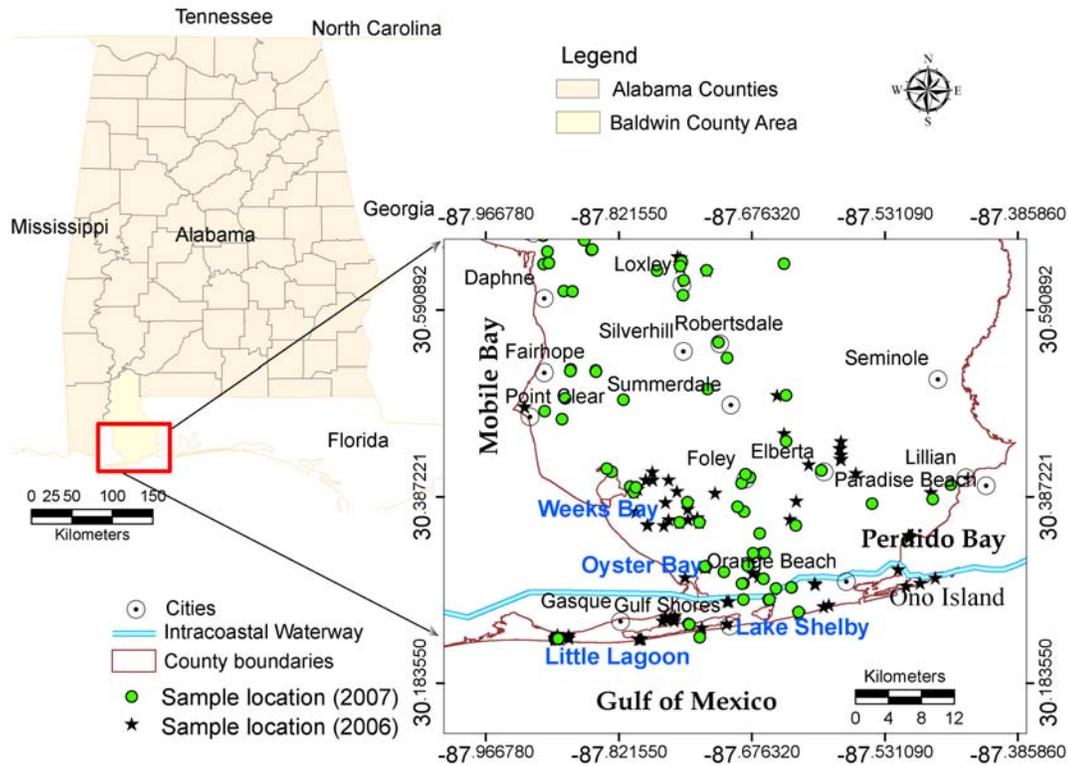
Baldwin County is the largest county in Alabama, comprising an area of approximately 4,130 km<sup>2</sup>. The research area encompasses an area of 1,626 km<sup>2</sup> in Southern Baldwin County. The study area is located South of Interstate 10 and is bounded to the South by the Gulf of

Mexico and to the West, Southeast, and East by Mobile Bay, Perdido River, and Perdido Bay, respectively (Fig. 7). This region includes some of the fastest growing communities (e.g., population and development) in the region including Fort Morgan Peninsula, Gulf Shores, Orange Beach, and Perdido Beach.

#### Population and Land-use/Land-cover

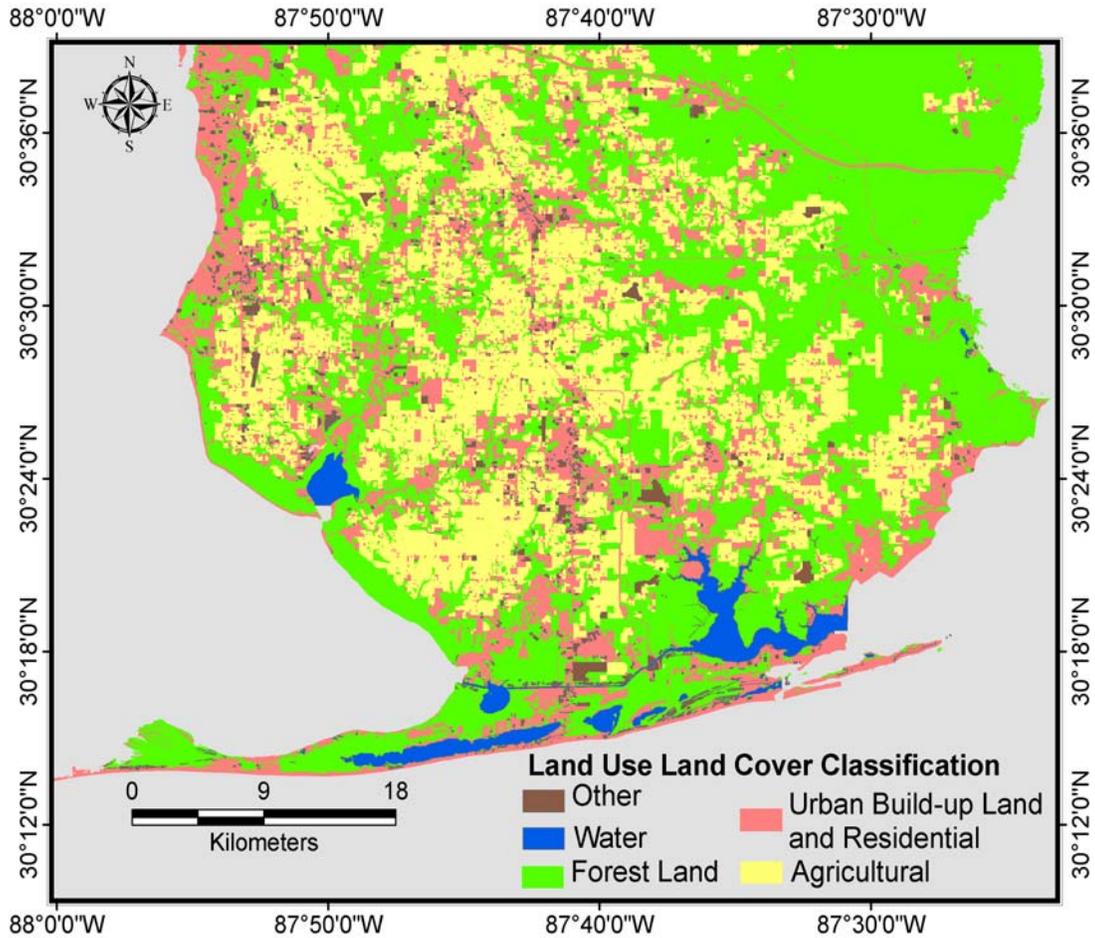
The population of Baldwin County increased significantly from the year 2000 with the highest rates reported for Fort Morgan Peninsula, Gulf Shores, Orange Beach, and Ono Island. Baldwin County has one of the highest population increases in Alabama, second only to Shelby County. As a result of increasing population, tourism, and development, groundwater pumping in the region increased from 2.7 9 10<sup>7</sup> to 1.6 9 10<sup>8</sup> L/day between 1966 and 1995 (Reed 1971; Reed and McCain 1971; Robinson et al. 1996).

Land use in Baldwin County varies considerably (Fig. 8). The major types of land-use include agriculture, forest, urban build-up, and residential. Agriculture makes up a significant percentage (approximately 40%) of the land-use/land-cover within the study area (USGS 2004). In the southernmost part of the study area, (i.e., Gulf Shores, Orange Beach, and Perdido Beach), recreational land-use accounts for a relatively large percentage of the area (Fig. 8).



**Fig. 7** Location of study area and surveyed groundwater wells (2006 and 2007)

It is important to consider land-use/land-cover relationships and changes when assessing nitrate levels and identifying potential sources contributing to groundwater contamination in the region. Current changes of land-use/ land-cover patterns can be extremely useful for identifying sources of nitrate to groundwater such as agricultural distribution and areas in which septic systems are widespread. It can be observed that the central and northern portions of the study area are dominated by agriculture with sparse residential development (Fig. 8). In contrast, areas adjacent to Mobile Bay, Weeks Bay, Little Lagoon and southern portions of the study area in close proximity to the Gulf of Mexico are dominated by suburban and rural residential land-use.



**Fig. 8** Distribution of major land-use land-cover classes for Southern Baldwin County, AL, (modified from the 2004 Baldwin County, USGS Land Use Land Cover classification)

### Stratigraphy and Hydrogeology

The stratigraphy of Southern Baldwin County, as well as that of coastal and offshore Alabama, consists of a relatively thick Jurassic to Holocene sedimentary sequence (Chandler et al. 1985). At relatively shallow depths, interbedded sands, silts, gravels and clays comprise the middle Miocene to Holocene sedimentary rocks which hosts the freshwater aquifer zones of Baldwin County area. The thickness of these sediments regionally decreases towards the Gulf of Mexico. The fresh groundwater resources of coastal Baldwin County occur in four principal aquifers. The upper unit, known as the Beach Sand Aquifer or Aquifer Zone A1, is an

unconfined aquifer consisting of white fine- to coarse-grained quartzose sands, silt, and locally sandy clay. The middle unit, known as the Gulf Shores Aquifer or Aquifer Zone A2, varies from confined to semi-confined to unconfined throughout the extent of the study area. The aquifer is extensively developed as a source of fresh water for municipal, industrial, private and irrigation wells. Recharge to this aquifer zone occurs from rainfall, where the unit crops out to the North under unconfined conditions (Chandler et al. 1985) and is more vulnerable to surface contamination. The lower unit is known as the Deep Miocene Aquifer or Aquifer Zone A3. This hydrologic unit is similar to Aquifer A2 in terms of lithology, with the exception that the sand and clay layers are more defined. Groundwater is typically present under confined or artesian conditions. Increasing numbers of the public water supply wells continue to be completed within this aquifer due to its limited exposure to sources of surface contamination. However, it should be noted that in the area of Fort Morgan Peninsula, the unit is infiltrated with saltwater, (Chandler et al. 1985; Gillett et al. 2000) and therefore, cannot be used as a resource of potable water in this most southernmost part of Baldwin County. The aquifer receives recharge from precipitation and resulting infiltration where the confining unit thins out and the aquifer unit crops out into the northern part of the study area. Aquifer characteristics, such as transmissivity and hydraulic conductivity, vary spatially throughout the study area as a result of variations in past depositional settings.

Groundwater flow direction is primarily towards areas of active discharge such as wells and large bodies of water such as Gulf of Mexico, Bon Secour River, Bon Secour Bay, and Oyster Bay. Hence, the general direction of regional groundwater flow is South, South-Southeast and South-Southwest depending on the regional discharge zones. Recharge is directly influenced by precipitation and infiltration rates, which are subject to dramatic fluctuations during periods

of little to no rainfall and/or during severe drought conditions. A detailed description of the hydrogeology and groundwater occurrence and a generalized hydrogeologic cross section of the study area is presented by Murgulet and Tick (2007).

### **Methodology**

To meet the objectives of the research, geologic and hydrogeologic information coupled with groundwater nitrate concentrations were collected and compiled to generate spatial distribution and contamination maps. Such integration allows for meaningful identification of the areas contaminated and most vulnerable to nitrate contamination. For the purposes of this study, it should be noted that the maximum contaminant level (MCL) for nitrate, established by the USEPA (1996), is 45 mg/L (as nitrate) which is equivalent to 10 mg/L nitrate (as nitrogen). Once these MCLs are exceeded, the water is no longer acceptable (in terms of health) for drinking water purposes and additional water treatment is needed or well abandonment or discontinued operation is required.

#### Data Collection

During a 2-year period beginning in 2006 and through 2007, groundwater samples were collected from public supply wells, private supply wells, and industrial and irrigation groundwater wells. The spatial locations (i.e., longitude and latitude) of surveyed wells were recorded using GPS (Fig. 7). Surveyed wells were monitored for water level (hydraulic head) and well depth. In addition, a wealth of information and data was collected and gleaned from GSA, ADEM, local water utilities, golf courses, agricultural farms, and numerous other businesses and private well owners across Southern Baldwin County.

## Sample Analysis

Groundwater samples were analyzed for nitrate concentrations and other geochemical parameters. These parameters were chosen, because they are potential indicators of pollution from agricultural practices (e.g., nitrate and chloride). Approximately 100 wells were sampled during the 2-year period. Samples were filtered, preserved, and analyzed within prescribed maximum holding times. All samples represent raw water samples collected from taps at the wellhead (after purging). Groundwater chemical field parameters including conductivity, resistivity, ORP, pH, and temperature were measured using a portable field multi-meter (Ultrameter II 6P, Myron L Company). The nitrate ( $\text{NO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) concentrations were analyzed using a Dionex High Performance Ion Chromatograph (Model DX600, Dionex Corp., Sunnyvale, CA) equipped with an autosampler, an anion-exchange column (7 mm, 4 9 250 mm; Dionex AS14A), and a conductivity detector (Dionex CD25), housed within the Geochemical Analytical Facility at the University of Alabama. The lower detection limit of the method was approximately 0.01 mg/L. For ion chromatograph (IC) analyses, nitrate samples were first removed from the refrigerator, allowed to equilibrate to room temperature and analyzed using a multi-point standard curve and diluted as necessary to remain within the linear range of the instrument. To provide confidence in the sample analyses and the accuracy of the instrument, the nitrate samples were run in triplicate to assure consistency of the results.

## Geographic Information System (GIS)

All data relevant to the nitrate contamination of groundwater were collected-including for instance, but not exclusively-topography, geology, land-use/land-cover, hydrology, hydrogeology, and rainfall amounts. ArcGIS was used to compile the geospatial data, to record and map well locations, well depths, hydrogeological information, and concentration data

collected from fieldwork, which allowed for the generation of iso-concentration maps and groundwater elevation and flow maps. The spatial database for the project was built in the raster and vector formats inside the GIS. The output maps elaborated for this study are shown in Figs. 9, 10, and 11. The grid layer for depth to water and saturated thickness of Aquifer Zone A2 was generated by computer subtraction of water-level elevation data sets from land surface elevation. Land surface elevations were derived from a Digital Elevation Model (DEM) for the Southern Baldwin County area. The water-level elevation data set was obtained from field measurements and from the groundwater well records available at GSA and ADEM.

Iso-concentration and groundwater elevation maps were prepared to determine areas impacted by high levels of nitrate and those areas which may be most vulnerable to nitrate contamination for Aquifer Zone A2. Nitrate concentrations in Aquifer Zones A1 and A3 were considerably lower than the established MCL; and therefore, the current study (i.e., iso-concentration maps) focuses upon nitrate concentrations within Aquifer Zone A2. The nitrate concentrations and groundwater level data were interpolated to construct the iso-concentration and groundwater elevation potentiometric surface) maps. ArcGIS software was used to interpolate the data and create the final output maps. To assure further confidence in interpolation schemes, the output maps were compared with the output maps developed from the same data using Surfer software package (Golden Software, Inc.) and compared with the actual concentrations and water levels measured from groundwater wells. The kriging interpolation method proved to be most effective at simulating iso-concentration and potentiometric surface contours when compared to the observed data distribution.

The output concentration grid layers for nitrate were reclassified in order to develop the final concentration maps that delineate only those sections exceeding regulatory MCLs for

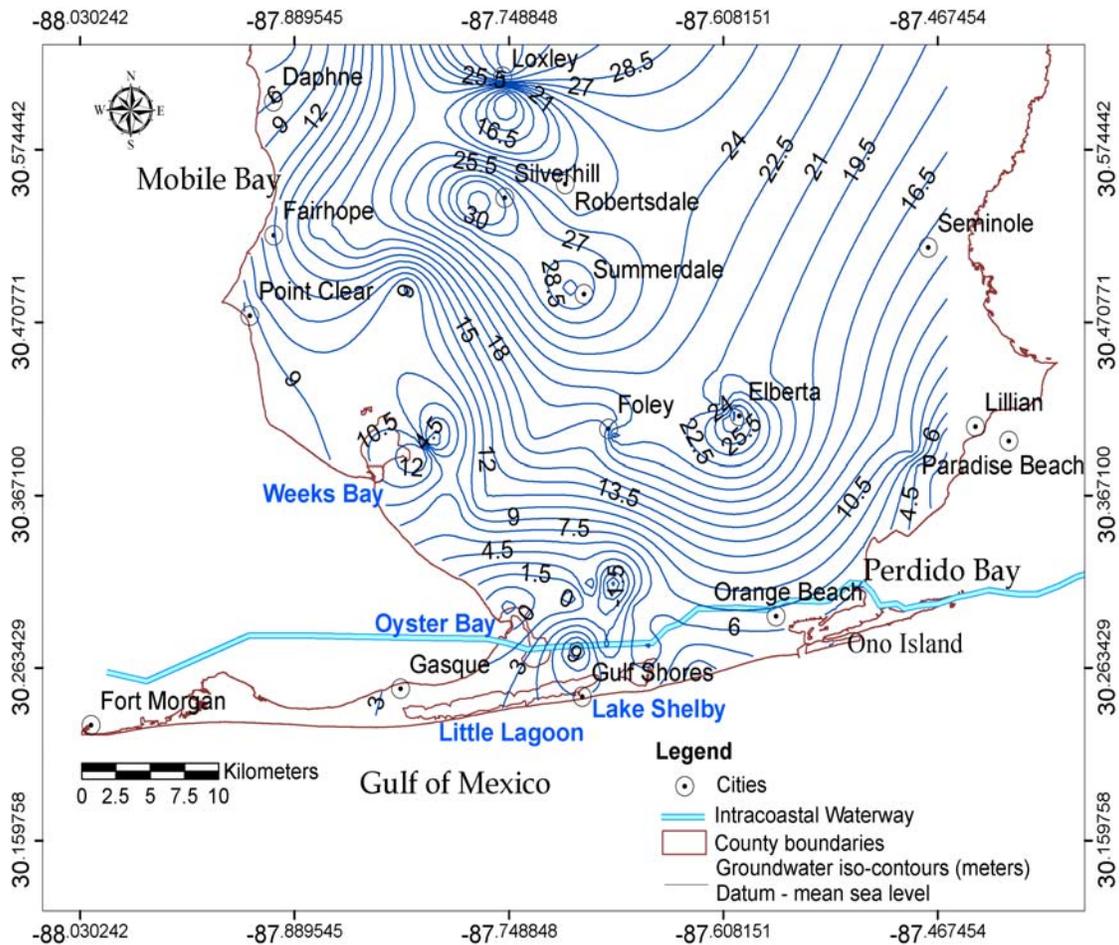
nitrate as deemed by the USEPA (1996) (Fig. 10a, b). The reclassification process involved development of a new raster layer by changing the attribute values of the cells of the input layers. Through this process, critical areas such as those that exceed the 45 mg/L nitrate limit were identified.

The groundwater elevation map was constructed to determine the dominant local and regional groundwater flow directions. Groundwater elevation contours (i.e., potentiometric surface contours) for Aquifer Zone A2 are shown in Fig. 9.

## **Results**

### **Regional and Local Groundwater Flow**

A groundwater elevation map constructed from the collected water level data between 2006 and 2007 provided the current state of regional and local groundwater flow of Aquifer A2 for the study area (Fig. 9). The general groundwater flow for all aquifer zones (A1, A2, and A3) for the study region was determined to be predominantly South, South-Southwest, and South-Southeast. Due to the fact that observed elevated nitrate levels were most significant in Aquifer Zone A2, this study focused on the hydraulic conditions (i.e., groundwater flow) within this aquifer unit. For Aquifer Zone A2 specifically, groundwater flow direction trended East, Southeast, South and Southwest with hydraulic gradients of approximately 0.0006, 0.0013, 0.0013, and 0.0016, respectively, and relatively steeper hydraulic gradients observed in the South, Southwest and Southeast directions (Fig. 9).



**Fig. 9** Groundwater elevation map for Aquifer Zone A2; datum, mean sea level

### Groundwater Availability and Nitrate Contamination

The availability of groundwater for public and private use is primarily dependent upon the volume capacities of the aquifer itself. However, in regions which are vulnerable to nitrate contamination, large volumes of water can be rendered unsuitable for use due to degraded water quality which exceed regulatory health limits (i.e., MCL = 45 mg/L as nitrate). Maximum and average values of nitrate concentration for Aquifer Zone A2 are included in Table 2. Iso-concentration maps are presented, displaying the zones impacted by elevated levels of nitrate (Figs. 10, 11). It is important to recognize that the iso-concentration maps utilize interpolation

schemes (i.e., kriging) based on available data. Due to the fact that some areas within the region lack any well data, concentrations of nitrate may not be revealed in those specific areas within the figures. Hence, it should be clear that these apparently “non-impacted” regions may in reality possess elevated levels of nitrate.

#### 2006 Groundwater Nitrate Data

Along the narrow coastal zones of the study area (along the Gulf of Mexico), slightly elevated concentrations of nitrate were observed in only a very small portion of Aquifer Zone A1 in close proximity to Perdido Bay. Based on the 2006 Aquifer A1 groundwater survey data, the average nitrate concentration (as nitrate) for Aquifer Zone A1 was determined to be 3.71 mg/L with a maximum concentration of 37.67 mg/L in close proximity to Perdido Bay. Although the 2006 groundwater samples collected from Aquifer Zone A1 exhibited slightly elevated levels of nitrate confined to a very small spatial extent (i.e., Perdido Bay), it was revealed that nitrate concentrations did not exceed the regulatory MCL (45 mg/L). However, the maximum concentration was observed to be close to the regulatory limit.

Aquifer Zone A2, a principal water bearing aquifer for Baldwin County, has been extensively developed for domestic, agricultural, municipal, and industrial uses. Groundwater in Aquifer Zone A2 exhibited elevated nitrate concentrations, and it can be observed that nitrate contamination was quite extensive throughout a significant portion of Southern Baldwin County (Fig. 10a).

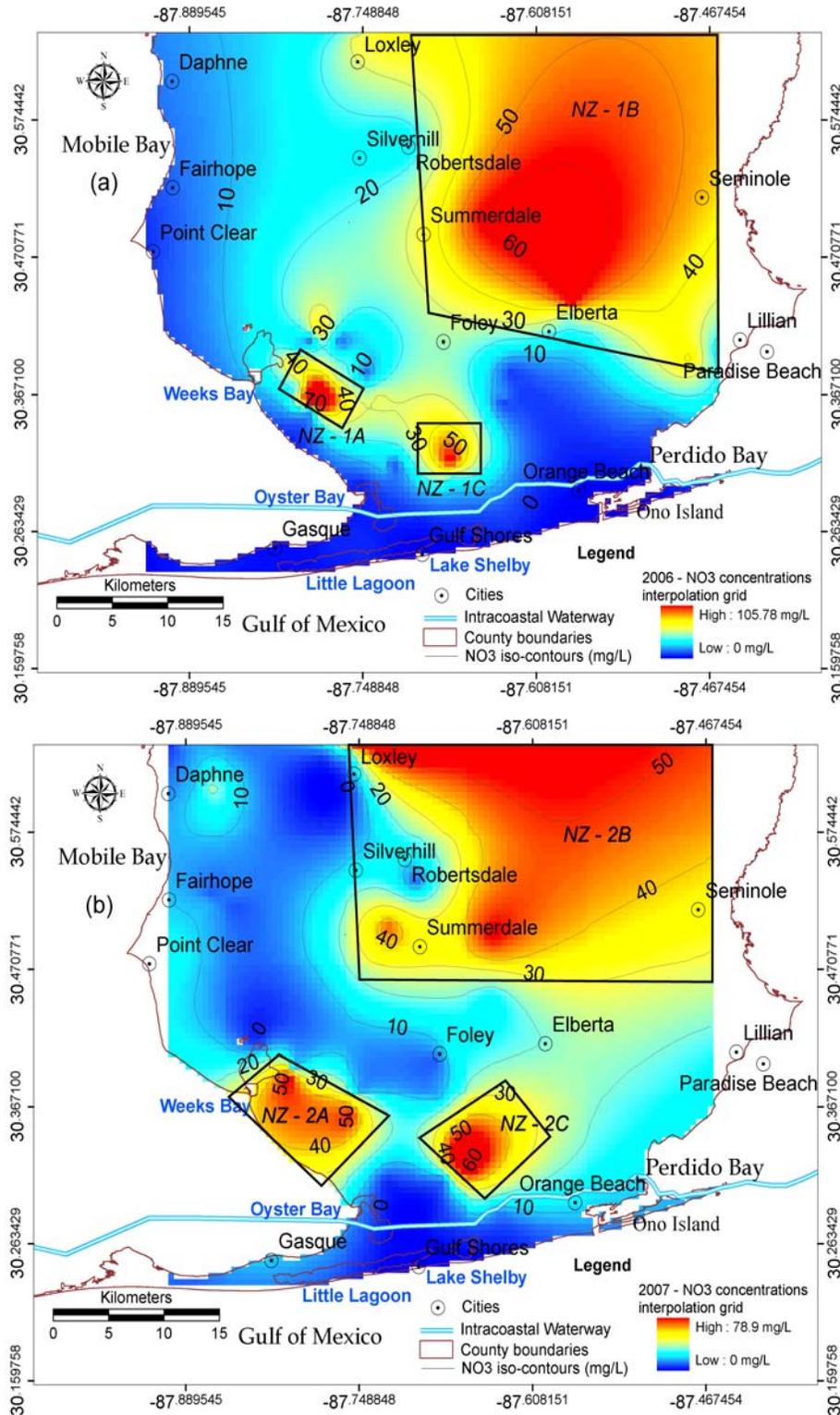


Fig. 10 Iso-concentration maps and potential nitrate source zone locations: a) Aquifer-Zone A2, 2006 nitrate concentrations; b) Aquifer-Zone A2, 2007 nitrate concentrations; concentrations are in mg/L; the contour interval is 10 mg/L

Based on a thorough sampling of the wells in the region for the year of 2006, the average nitrate concentration for Aquifer Zone A2 was determined to be 22.73 mg/L with a maximum concentration of 121.37 mg/L just East of Weeks Bay and South of Hwy 98 (nitrate zone NZ-1A) (Fig. 10a). Other “hot-spots” or zones with elevated concentrations of nitrate exceeding regulatory limits (i.e., MCLs) include a relatively large area surrounding and adjacent to Loxley, Summerdale, Elberta, Seminole, and Paradise Beach, and an area about 8 km East of Oyster Bay between Foley and Gulf Shores. Of these “hot-spots”, the most extensive area (nitrate zone NZ-1B) with elevated nitrate levels or nitrate zone (i.e., average % 45.39 mg/L; maximum % 63.16 mg/L) includes the central and northeastern portion of the study area bounded by Loxley to the North, Robertsdale to the West, Seminole to the East, and Elberta to the South (Fig. 10a). The smaller “hot-spots” include the areas just East of Weeks Bay and South of Hwy 98 (nitrate zone NZ-1A) with an average and maximum nitrate concentration of 37.85 and 121.37 mg/L, respectively; and the area about 8 km East of Oyster Bay between Foley and Gulf Shores along Hwy 59 (nitrate zone NZ-1C) with an average and maximum nitrate concentration of 33.78 and 63.74 mg/L, respectively.

Groundwater samples collected from the deeper Aquifer A3 exhibited relatively low nitrate concentrations. The average and maximum nitrate concentrations observed within this aquifer for the year of 2006 are 0.50 and 3.13 mg/L, respectively. The presence of nitrate indicates that the potential for contamination of this aquifer exists.

Table 2. Results of nitrate analyses from groundwater by hydrogeologic unit over a two-year study period (2006 and 2007)

Regions of elevated nitrate concentration	Year 2006		Regions of elevated nitrate concentration	Year 2007		Potential Source
	Hydrogeologic Unit			Hydrogeologic Unit		
	Aquifer Zone A2			Aquifer Zone A2		
	High	Average		High	Average	
NZ-1A	121.8	37.9	NZ-2A	80.8	31.2	Residential/septic
NZ-1B	62.2	45.4	NZ-2B	63.1	27.8	Agriculture inputs
NZ-1C	63.7	33.8	NZ-2C	53.4	29.5	Agriculture inputs

Nitrate MCL established by USEPA = 45 mg/L NO<sub>3</sub>; or equivalently 10 mg/L NO<sub>3</sub> (as nitrogen)

Elevated chloride concentrations were observed to accompany the most elevated nitrate concentrations for each of the nitrate zones. However, the highest density of points that exhibited both elevated nitrate and chloride concentrations were focused within the circled regions (S.I and S.II) in nitrate zone NZ-1A (Fig. 12a). The maximum chloride concentration was 51.1 mg/L and the average chloride concentration was 12.48 mg/L. The second highest chloride concentration (40.4 mg/L) accompanied by high nitrate concentration (37.03 mg/L) was recorded for nitrate zone NZ-1B in the central northwestern portion of this region. The average chloride concentration for the surveyed study area excluding the points located within the coastal saltwater impacted areas was 8.76 mg/L.

#### 2007 Groundwater Nitrate Data

Elevated nitrate levels in groundwater were absent in the narrow coastal zones of the study area (along the Gulf of Mexico) within Aquifer Zone A1, as observed from the data collected in between 2006 and 2007 (Fig. 10b). It should be noted that not all of the same sampling locations conducted in 2006 were available for sampling during the 2007 collection

period within Aquifer Zone A1. Therefore, a comparison between the 2-year data can only be conducted for a small area in Fort Morgan. However, it is important to recognize these overall trends and be aware that the presence of nitrate within this aquifer may be a concern and should be regularly monitored. The 2007 data for Aquifer Zone A1 exhibits the presence of slightly increased nitrate concentrations for the Fort Morgan area. The average and maximum nitrate concentrations for this zone are 7.62 and 11.78 mg/L, respectively.

Similar to the 2006 data, the 2007 analysis for Aquifer Zone A2 revealed elevated levels of nitrate in several consistent regions throughout the study area but to different extents. An area bounded by the eastern shore of Mobile Bay to Oyster Bay on the South and inland from Weeks Bay (nitrate zone NZ-2A) exhibited an average nitrate concentration of 29.50 mg/L with maximum concentrations of 53.40 mg/L (Fig. 4b). Elevated levels of nitrate were also observed in a relatively large area in Aquifer Zone A2 within the central and north-eastern portion of the study area (nitrate zone NZ-2B), extending from Loxley to the South of Robertsdale, to just South of Summerdale and extending as far East as Seminole. The average nitrate concentration in this region was 27.79 mg/L with maximum concentrations of 63.12 mg/L. For the year of 2007, the area with the highest nitrate concentrations (80.79 mg/L) was observed approximately 8 km East of Oyster Bay between Foley and Gulf Shores along Hwy 59 (nitrate zone NZ-2C). The average and maximum nitrate concentrations for this zone are 31.19 and 80.79 mg/L, respectively.

The 2007 data indicated low nitrate concentrations in Aquifer Zone A2 along the Gulf of Mexico as were reported for the year of 2006. Analysis of the 2007 data for the deeper Aquifer Zone A3 indicate the presence of very low nitrate concentrations with an average concentration of 0.70 mg/L and a maximum concentration of 4.21 mg/L at the same location where the

maximum concentration for the 2006 data was measured. Similar to the data collected in 2006, elevated chloride concentrations were observed to accompany the most elevated nitrate concentrations for each of the nitrate zones. The 2007 data revealed that nitrate zone NZ-2B, in the central northwestern portion of this region, exhibited the highest coupled nitrate and chloride concentrations. A maximum chloride concentration (35.74 mg/L) and nitrate concentration (63.12 mg/L) in this area were measured from the same well and these data plot within the circled region (S.I) in Fig. 6b. The NZ-2A zone still proved to have highest density of points within the circle regions (S.I and S.II), consistent with the NZ-1A 2006 data (Fig. 11b) that also exhibited high coupled nitrate and chloride concentrations. The maximum chloride concentration was 22.06 mg/L and the average chloride concentration was 9.29 mg/L. The average chloride concentration for the surveyed study area excluding the points located within the coastal saltwater impacted areas was 10.72 mg/L.

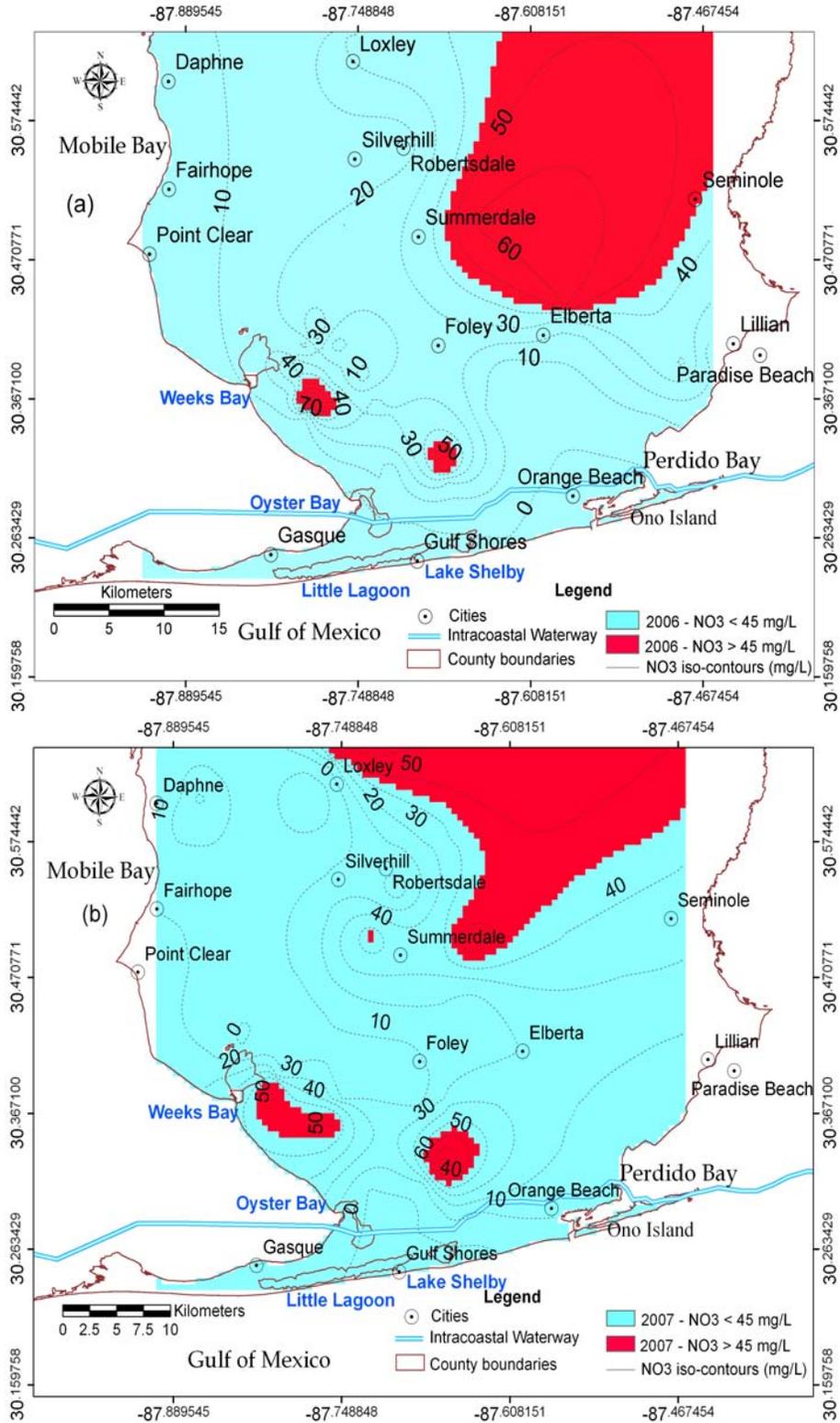
## **Discussion**

### Temporal Changes

Temporal changes of nitrate concentrations were observed from analyzing groundwater samples in the aquifers underlying Southern Baldwin County over two consecutive years (i.e., 2006 and 2007). It is expected that groundwater flow conditions will vary from year to year, dependent upon factors such as the amount of precipitation, amount of regional pumping from the aquifers, seasonality changes in hydraulic gradient, and changes in recharge and discharge. Therefore, it is not surprising that nitrate levels may be influenced by local and regional dynamics of groundwater flow affecting variation in nitrate concentration throughout the year or from year to year.

In Aquifer Zone A1, nitrate concentrations in close proximity to the Gulf of Mexico (i.e., Fort Morgan Peninsula) tend to increase from the first sampling event (2006) to the second (2007) based only on the same sampling points for the 2 years. The 2006 and 2007 data for Aquifer Zone A2 indicated that the relatively smaller “hotspot” (NZ-1A) of elevated nitrate concentrations (2006 data) located just East of Weeks Bay was observed to have increased in extent and decrease in concentration (NZ-2A) along the eastern shore of Mobile Bay from Weeks Bay to Oyster Bay on the South. This apparent decrease in nitrate concentration and increase in extent may have occurred due to nitrate transport and re-distribution from nitrate concentrations observed further inland.

The elevated nitrate levels observed from the 2006 samples, may have been transported and discharged towards Mobile Bay, representing a snap-shot of the larger affected area at the latter sampling time (2007) (Fig. 10a, b). Another explanation for this increase in extent of nitrate within this area could be due to additional or relatively new sources originating within this broader region. A zone of elevated nitrate concentration (NZ-1C) observed from the 2006 data, located approximately 8 km East of Oyster Bay between the cities of Foley and Gulf Shores, was observed to extend in size and magnitude and increase in concentration over the 2-year period (NZ-2C). This may either be explained by nitrate transport with transient groundwater flow, and/or simply related to natural changes or fluctuations with groundwater flow and nitrate re-distribution. In addition, the observed behavior within this zone may be related to an increased and constant input of nitrate from the land surface.



**Fig. 11** Groundwater contamination maps of nitrate concentration exceeding regulatory MCLs in groundwater: a) Aquifer-Zone A2, 2006 data; b) Aquifer-Zone A2, 2007 data

The most extensive zone (“hot-spot”) with elevated nitrate levels, located within the central and north-eastern region of the study area (surrounding Silverhill, Robertsedale, Summerdale, and Seminole) (NZ-1B), was observed to decrease slightly in extent but remain constant in concentrations over the 2-year period (NZ-2B) (Figs. 10a, b, 11a, b). As previously mentioned, this may be related to flushing or dilution effects from transient groundwater flow, to temporal inputs of nitrate to the groundwater system (i.e., seasonal or annual), in-situ attenuation process (physical/ biological degradation, and/or consumption), changes due to re-established flow pathways and hydraulic gradients, and/or discharge to Mobile Bay and the Gulf of Mexico.

Aquifer Zone A3 has been extensively developed for municipal uses. Many of the public water supply wells are completed within this aquifer unit due to its limited vulnerability to sources of surface contamination. As part of this current study, limited data were available for the year of 2006 and therefore, iso-concentration maps for nitrate are not provided for this aquifer. Even though groundwater samples obtained from wells completed in Aquifer Zone A3 exhibited very low nitrate concentrations, it should be noted that Aquifer Zone A3 can be susceptible to nitrate contamination by transport via downward hydraulic gradients, improperly installed wells (i.e., “short-circuiting”), vertical downward migration through discontinuities between the confining aquitard units (i.e., conduits for exchange and transport), and/or from contaminated groundwater directly recharging Aquifer Zone A3 from sources further north. Due to the fact that nitrate is often attributed to surface sources of contamination (i.e., leaking septic systems, agricultural applications, etc.) it may be expected that significant nitrate contamination would first be observed in the surficial or upper aquifers in the area. Further study and evaluation of nitrate contamination within Aquifer Zone A3 is needed before any conclusive statements about its groundwater quality can be made.

The groundwater contamination output maps (Fig. 11a, b) delineate only those zones within the study (Aquifer Zone A2) area which exceed regulatory limits (i.e., MCLs) of nitrate in drinking water. As expected, the nitrate concentrations exceeding regulatory limits occur within the same associated nitrate “hot-spots” discussed previously. The spatial distribution of nitrate exceeding regulatory drinking water standards over the 2-year analysis period suggests that these zones may be locations of continued sources. Although spatial distribution varies somewhat over this time period, the general trend of the observed high nitrate concentration may be a concern for the region’s water supply. Continued monitoring of groundwater wells in the region will be important to verify if these locations are in fact sources of contamination or if these nitrate concentrations are transient through time.

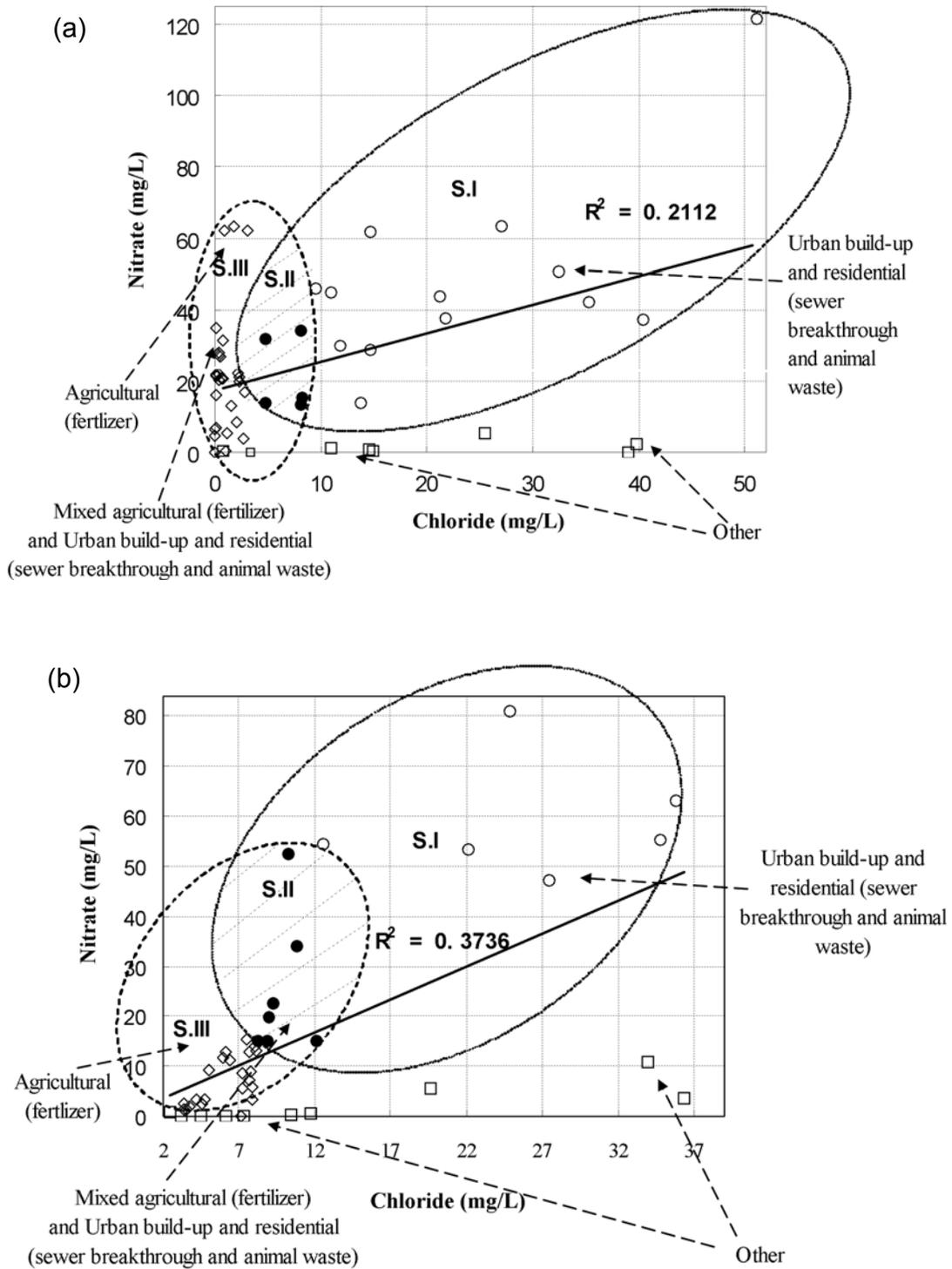
Variation in nitrate concentration and spatial distribution can be affected by the local and regional groundwater flow system. Upon analysis of the groundwater elevation map for Aquifer Zone A2, it can be observed that dominant groundwater flow pathways trend towards major discharge points to Mobile Bay on the West, Gulf of Mexico to the South, and Perdido Bay on the East. This may explain how such an extensive zone of nitrate contamination evolved from affected wells within the north-central portion of the study area. The general eastward flow direction towards Perdido Bay in this region is consistent with the observed extensive nitrate trend which appears to be spreading eastward. This may be a concern as nitrate levels can reach potential water supply wells or discharge into Perdido Bay affecting the local ecological health of these coastal systems. In addition, zones impacted by elevated levels of nitrate in Aquifer Zone A2 were observed to spread within the western and southern portions of the study area. Upon a similar analysis of the groundwater flow direction in Aquifer Zone A2, it appears that nitrate in these areas may be transported with groundwater. It can be observed in the iso-

concentration maps that a nitrate zone in the western portion of the study area appears to spread and discharge into Weeks Bay and Mobile Bay. Similarly, an elevated nitrate zone in the southern portion of the study area may be extending further as it is influenced by the southerly flowing groundwater that eventually discharges to the Gulf of Mexico.

### Potential Sources

The analyses of nitrate and chloride concentrations from groundwater samples collected over a 2-year period indicates that there may be several regions within Southern Baldwin County serving as sources of nitrate or with recurring elevated concentrations of nitrate. The prolonged elevated concentrations of nitrate observed within the groundwater system may be a cause of concern posing risks of contamination to water-supply wells and surface water bodies in the region. Although it is easy to understand health risks associated with nitrates in drinking water, it should also be recognized that nitrate concentrations discharging to surface water bodies (i.e., coastal estuaries, bays, streams, and lakes) can directly lead to eutrophication and hypoxia, degrading natural habitats and economies that depend upon a healthy and productive ecosystem (i.e., fishing/shrimping industry, tourism, etc.).

As observed in the nitrate iso-concentration maps for Aquifer Zone A2 over the 2-year study period, the central and north-eastern region (surrounding and comprising Silverhill, Robertsdale, Summerdale, and Seminole) (NZ-1B and NZ-2B) of the study area was impacted most extensively with elevated nitrate levels (Fig. 10a, b). Although nitrate extent decreases slightly over the 2-year period, it is evident that there is a substantial nitrate input, suggesting that this zone may be a potential nitrate source. It may also be that this area experienced elevated nitrate concentrations from other sources outside the extent of the study area.



**Fig. 12** Source identification based on the nitrate and chloride concentrations and land-use/land-cover classification: a) year of 2006; b) year of 2007

Over the 2-year study period, the highest nitrate concentrations within Aquifer Zone A3 were also observed within this same zone and were noticed to increase slightly from 3.13 mg/L in 2006 to 4.21 mg/L in 2007. This may be an indication that sources within Aquifer Zone A2 have infiltrated into the deeper Aquifer Zone A3 within this area. The modified 2004 USGS land-use/land-cover classification (Fig. 8) shows this area to be dominated by agriculture. Therefore, it is reasonable to consider that agriculture within the circled region on (S.III) in Fig. 11 is likely the dominant source of the nitrate levels in Aquifer Zones A2 and A3 in the region. However, the increased nitrate and chloride concentrations for the most north-western part of this zone may suggest the presence, to a limited extent, of alternative sources such as sewer breakthrough and/or animal waste as some of the data fall within the circled regions (SI and S.II) of Fig. 11.

A relatively small in extent nitrate “hot-spot” (NZ-1C and NZ-2C) can be observed in the area between Foley and Gulf Shores (Fig. 10a, b). Although localized and fluctuating in size and concentration over the 2-year study period, this “hot-spot” remains stationary indicating that there may be a continued input of nitrate at this locale. The land-use pattern in this area was determined to be dominantly agriculture and to a smaller extent, urban build-up land and residential (USGS 2004). For this reason, it is suspected that the elevated nitrate levels observed in this region is most likely related to agricultural practices and to some extent to leaking, outdated, and/or improperly installed septic systems.

In the southwestern portion of the study area, another relatively small (in extent) nitrate “hot-spot” can be observed just East of Weeks Bay (NZ-1A). Over the period of the 2-year study, the extent of nitrate contamination increases in scale, impacting a significantly larger spatial area (NZ-2A) with a reduction of concentration over time (Fig. 10a, b, 11a, b). This

indicates that this zone within the vicinity of Weeks Bay may be a source of nitrate which has led to an increased spatial extent of contamination downgradient as groundwater flows and discharges to Mobile Bay along the coastline from Weeks Bay to Oyster Bay. In addition, it may be that other sources closer to the coastline have emerged causing a notable increase in the spatial extent of nitrate in groundwater. Another explanation for this behavior may be that sources further inland have redistributed nitrate concentrations over a larger extent within this vicinity during this time period. Current land-use patterns are dominantly residential within this area (USGS 2004) supporting the fact that the nitrate sources are likely related to sewer breakthrough from leaking, outdated, and/ or improperly installed septic tanks. The chloride and nitrate concentrations for points located within this zone are consistent with contamination derived from sewer breakthrough and animal waste (Fig. 11a, b) and to some extent from the application of fertilizers (Fig. 11a, b).

### **Conclusions**

The groundwater system of Southern Baldwin County is comprised of three hydraulically distinct aquifers that will likely provide ample supply if properly managed. However, nitrate contamination of groundwater may be a concern for the study area. The results of this study indicate that spatially extensive nitrate concentrations exceeding regulatory limits (MCL = 45 mg/L as nitrate) were present within Aquifer Zone A2 in Southern Baldwin County, Alabama over a 2-year study period. In addition, slight degradation of groundwater quality due to the presence of nitrate was observed for the surficial coastal Aquifer Zone A1 and to a smaller extent for the deeper Aquifer Zone A3. Iso-concentration maps for Aquifer A2 demonstrate that three spatially distinct regions within the study area may serve as sources of nitrate or have, at the very least, remained impacted by relatively high nitrate concentrations. Current land-use distributions

coupled with nitrate–chloride correlation analyses were used to determine potential sources of nitrate to the groundwater system. For the most part, the overall nitrate–chloride correlation was not significant for the samples collected over the 2-year study which suggests that the major source of nitrate for the surveyed area is likely associated with the application of fertilizers. However, elevated levels of nitrate and chloride occurring together may suggest the presence of some alternative sources for a few of the other nitrate zones within the study area. It is important to note that it is difficult to definitively conclude the origin and type of sources without further evidence. Ongoing studies using nitrogen, oxygen, and carbon isotopes are being conducted to better assess the types of sources and contributions of nitrate to the groundwater and surface water systems of Southern Baldwin County. Although a large number of wells were sampled and analyzed to define the extent and magnitude of nitrate contamination in the aquifers of Southern Baldwin County, a denser network of wells from all aquifer zones need to be identified and monitored to gain higher spatial and temporal resolution. Further monitoring of the nitrate levels is necessary to evaluate the temporal evolution and distribution of nitrate concentrations within the aquifers underlying the region. Proper well placement and routine water quality monitoring is important to prevent Aquifer Zones A1, A2, and A3 from experiencing such problematic conditions associated with nitrate contamination. ArcGIS proved to be a valuable tool used to determine the spatial extent and magnitude of nitrate contamination of groundwater. Furthermore, the use of these tools provides an opportunity to assemble, standardize, and analyze scientific data that comes from a variety of sources, making it available to others who may be able to continue with further research studies.

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A NOVEL ISOTOPIC APPROACH TO DETERMINE SOURCES AND FATE OF NITRATE  
IN THE AQUIFER SYSTEM UNDERLYING SOUTHERN BALDWIN COUNTY,  
ALABAMA:  $\delta^{15}\text{N}$  AND  $\delta^{18}\text{O}$

**Abstract**

The contamination of groundwater with nitrate has become a major problem throughout the world. These related problems are often the result of anthropogenic activities, lack of management, and overdevelopment of water resources. Recently, a high level of interest has been generated in understanding and identifying the source and fate of nitrate in groundwater and surface water. Nitrogen and oxygen stable isotopes of groundwater nitrate, chloride/bromide ratios ( $\text{Cl}^-/\text{Br}^-$ ), nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4$ ), and land-use/land-cover (LULC) data were used in order to assess sources of nitrate to the groundwater system and determine the primary processes controlling the fate of nitrate in groundwater and contributions to the coastal surface waters in the study area. Isotope analyses of groundwater nitrate (e.g., nitrogen- $\delta^{15}\text{N}_{\text{NO}_3}$  and oxygen- $\delta^{18}\text{O}_{\text{NO}_3}$ ) indicate that nitrate in groundwater is primarily derived from the nitrification of ammonium in soil. Isotope and geochemical data analyses reveal that the presence of nitrate was likely the result of mixed end-members with signatures ranging from fertilizer to sewer and/or manure. However, analyses of land-use/land-cover and geochemical data suggest that groundwater signature is mostly influenced by nitrate sources originated from fertilizer application. Furthermore, isotope data indicate that denitrification was not an important process in this aquifer system. In the absence of denitrification and the presence of a permanent source, it is expected that the elevated groundwater nitrate concentrations will not be readily attenuated,

posing a potential contamination and degradation problem of coastal discharge zones (i.e. wetlands, estuaries, lagoons, and coastal lakes) into the future.

### **Introduction**

Contamination of groundwater due to nitrate has become a major concern for regions which rely solely on groundwater for drinking water purposes. Generally, it is considered that baseline concentrations of  $\text{NO}_3^-$  as nitrogen ( $\text{NO}_3^-$ -N) in groundwater are approximately 2 mg/L or below (Cook and Herczeg 1999). Groundwaters that exhibit concentrations above this limit are generally associated with anthropogenic pollution. Nitrate can contribute to the deterioration of water quality in agriculturally dominated and rural areas with heavy fertilizer and manure application and residential areas with improperly functioning septic systems. In aquifers where nitrate travels as a conservative contaminant, degradation of environmentally-sensitive ecosystems (i.e. coastal estuaries and wetlands) from excess nutrient loading may be ubiquitous. Furthermore, the presence of this contaminant in groundwater at greater depths provides an indication of recharge rates, dynamics of the aquifer, and identification and details about the source area.

In Southern Baldwin County, nitrate concentrations exceeding regulatory limits (Maximum Contaminant Level = 45 mg/L as nitrate) were identified within Aquifer Zone A2 and were primarily associated with areas extensively developed for agricultural and residential practices (Murgulet and Tick, 2008). In addition, slight degradation of groundwater quality due to the presence of nitrate was observed for the surficial coastal Aquifer Zone A1 and to a smaller extent for the deeper Aquifer Zone A3 (Murgulet and Tick, 2008). Dowling et al. (2003) investigated and quantified  $\text{NO}_3^-$  flux to the Gulf of Mexico. The study concluded that

groundwater discharge could have a high contribution to the nutrients loading to the Gulf of Mexico.

Groundwater quality is often linked to current land surface practices. A large majority of nitrate sources are anthropogenic of origin and are commonly confined to the same watershed and groundwater basin. Several studies indicate that the rural land uses, especially agricultural practices, can cause nitrate contamination of underlying groundwater (Vowinkel and Tapper 1995). In addition, regions experiencing significant population growth may be substantially contributing to the groundwater nitrate contamination (Bouwer 1978; Driscoll 1986; NRC 1993). Identifying sources and fate of nitrate in groundwater at a regional scale can be complicated and difficult to understand due to the mixing of nitrate from different sources and due to the extent to which denitrification occurs within an aquifer.

Isotopes are ideal tracers of groundwater and contaminant sources and evolution along flowpaths. Nitrogen isotopes have been predominantly used in environmental investigations to identify sources of nitrogen in surface water. Recently, the interest in using these isotopes has been extended to subsurface hydrology (Clark and Fritz 1997). Newly developed methods have recently combined utilizing nitrogen isotopes with the oxygen-18 ( $^{18}\text{O}$ ) isotope of nitrate as a complementary tool for nitrate source and fate identification (Bottcher et al. 1990). Not only they are used to identify sources of nutrient (e.g., nitrate, ammonia, and nitrogen) in waters, but they provide valuable information on the fate of nitrogen from the source to the sampling location. The combination of  $^{18}\text{O}$  and  $^{15}\text{N}$  provides a superior tool for the identification of nitrate sources allowing for the differentiation of sources and eliminating the effects of denitrification. This is based on the knowledge that different nitrogen sources have distinctive nitrogen and oxygen isotopic signatures.

Denitrification is a multi-step process that involves the chemical or biologically mediated reduction of nitrate to  $N_2$ . Through denitrification, fractionation of nitrogen and oxygen isotopes takes place. The lighter isotope of nitrogen  $^{14}N$  is preferentially consumed during the denitrification process causing the heavier isotope  $^{15}N$  to increase exponentially in the residual nitrate as nitrate is being consumed. Consequently, the acidity of the system will decrease (Kendall and McDonnell 1998). Furthermore, this will result in higher  $\delta^{15}N$  of nitrate values and overlapping signatures for different sources (Kendall and McDonnell 1998).

Generally, the extent to which the fractionation occurs is based on the abundance of nitrogen. In systems with low nitrogen, the fractionation is minimal. In the presence of large amounts of ammonium (e.g., application of artificial fertilizer), the process of nitrification is stimulated causing a large fractionation (Kendall and McDonnell 1998). Under this process, the  $\delta^{15}N$  value of the first-formed nitrate is relatively low compared to the pre-fertilization values (Feigin et al. 1974). However, as the ammonium concentration decreases, the nitrification rate, as well as the overall nitrification fractionation decrease causing the  $\delta^{15}N$  value of the total nitrate to increase towards pre-fertilization values (Feigin et al. 1974). Therefore,  $\delta^{15}N$  of groundwater or surface water nitrate is expected to be different than that of applied fertilizer.

In addition to stable isotope analyses, conservative chemical element ratios such as  $Cl^-/Br^-$ ,  $I^-/Cl^-$ , and  $F^-/Br^-$  can be used to trace groundwater sources. This is because their ratios are characteristic and well defined for different types of waters (e.g., rainwater, seawater, sewage water, etc.) (Kazemi et al. 2006). Conservative ions such as  $Br^-$ ,  $Cl^-$ ,  $I^-$ , and  $F^-$  are not subject to chemical reactions as water travels along different flowpaths and changing environmental conditions. Thus, their concentrations are dependent upon inputs from atmosphere and land surface, dissolution of materials, anthropogenic activities, and the presence of contaminants

already in the environment. Given the estimated concentration of each of these halogens in different contaminants and their conservative behavior, mass ratios can be used to identify and locate contamination sources. Chloride is the most abundant ion of the halogens but present in low concentrations in natural waters. Exceptions occur when a system receives inflow of water contaminated with seawater, sewage, or industrial waste. Alternative sources such as sewer breakthrough and animal waste can cause a significant increase of both nitrate and chloride concentrations (e.g., Canter and Knox 1985; Alhajjar et al. 1990; Robertson et al. 1991; Kehew et al. 1996; Hudak and Blanchard 1997). For example, the concentrations for septic tank effluent typically varies between 77 mg/L and 111 mg/L total nitrogen and 37 mg/L and 101 mg/L chlorides (Canter and Knox 1985). Bromide ( $\text{Br}^-$ ) originates naturally from precipitation and aerosols. Anthropogenic sources of  $\text{Br}^-$  come from auto emissions, stormwater, and fertilizer and pesticides (Lundstrom and Olin 1986; Wilde 1994). Therefore, while  $\text{Cl}^-$  concentrations alone offer information on the salinity increase,  $\text{Br}^-$  may indicate specific salinity sources. Thus, the ratio  $\text{Cl}^-/\text{Br}^-$ , offers valuable information in groundwater investigations.

The N stable isotopes approach to the  $\text{NO}_3^-$  sources identification has been used by several investigators to characterize the  $\text{NO}_3^-$  contamination problems in surface water and groundwater of many other regions (e.g. Kreitler 1975; Black and Waring 1977; Wolterink et al. 1979; Heaton 1986; and many others) but the technique has not been applied to Baldwin County. This study aims to identify the primary sources of nitrate to the groundwater system, determine the primary processes controlling the fate of nitrate in groundwater, and elucidate contributions to the coastal surface waters in a highly developed aquifer system predominated by agriculture and increasing residential development.



A combination of isotope and geochemical analyses were implemented to identify fate and sources of nitrate and to determine potential contribution of groundwater nitrate to the coastal surface waters and to the Gulf of Mexico. In addition, land-use/land-cover analyses were used to place constraints on the identification and location of the nitrate sources. The outcome of this study offers valuable information on estimating nitrate discharge to surface waters and to the Gulf of Mexico.

### **Background**

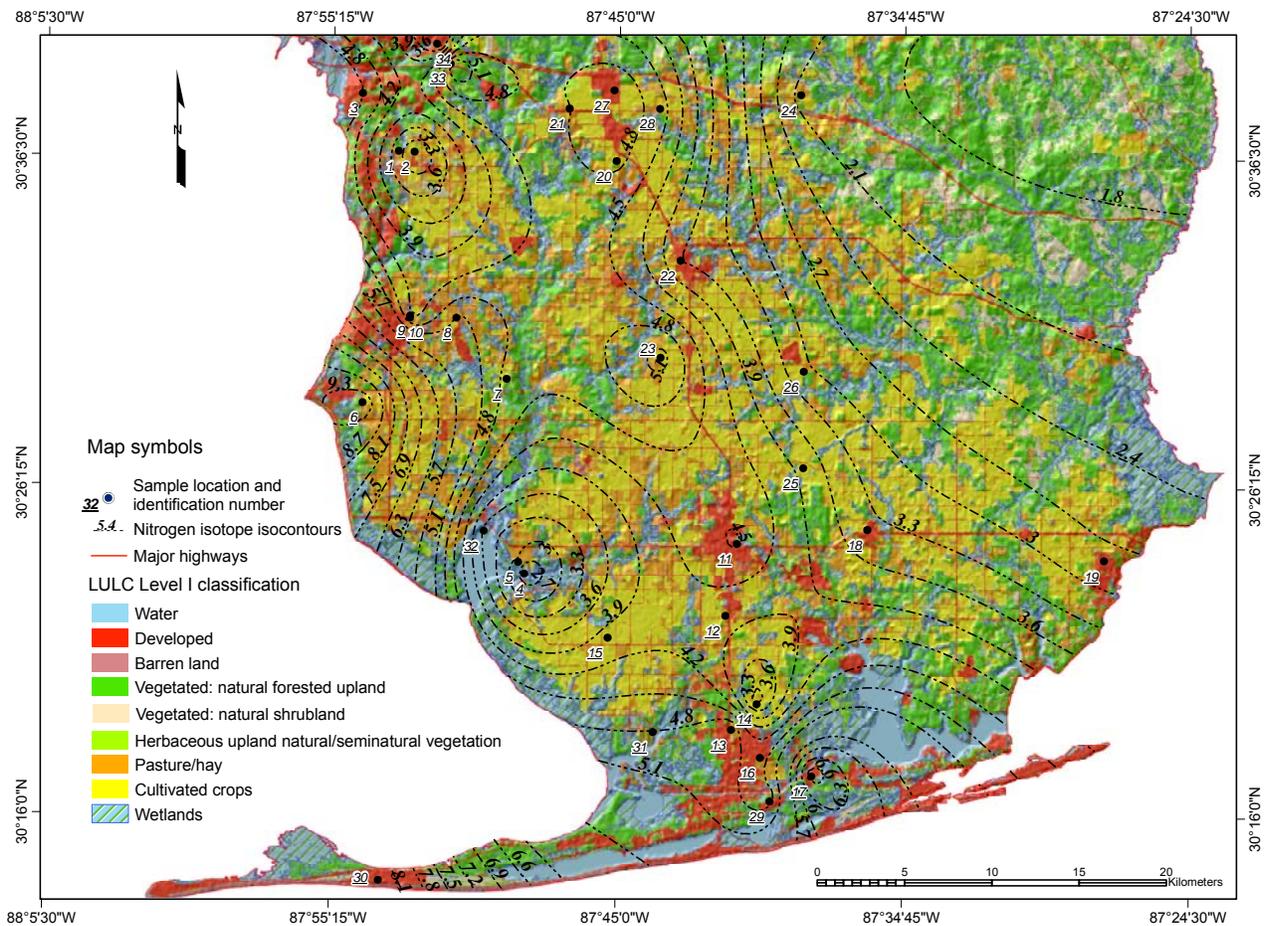
The study area, located in Southern Baldwin County, Alabama, South of Interstate 10, occupies an area of approximately 1,626 square kilometers (km<sup>2</sup>) and is bounded by the Gulf of Mexico on South and by Mobile Bay, Perdido River and Perdido Bay on the West, Southeast and East, respectively (Fig. 13).

The elevation in the study area follows a relative narrow range, from about 20 to 55 m above mean sea level in the North to sea level (0 m) along the coastal plain. Southern Baldwin County lies on the Coastal Lowlands district of the East Gulf Coastal Plain, a flat to gently undulating swampy plain (Walter and Kidd 1979). The soil of the area is mostly sandy and therefore precipitation infiltrates very rapid. Consequently, the runoff rates are very low, the flowing streams are absent, and direct precipitation infiltration to the water table aquifer is most likely to occur. The subsurface water flow generally follows the topography; groundwater moves from higher sandy plateau (the inland area) to the lower marshlands, to the Intracoastal Waterway, onto the coastal surface waters (e.g., Shelby Lakes, Little Lagoon, etc.) and Gulf of Mexico. During times when the evapotranspiration rates are high and/or the precipitation is minimal or absent, the water table is low and it slopes toward the Gulf of Mexico. Therefore, during these times, coastal waters will receive recharge from groundwater and to a small/negligible extent from precipitation and runoff.

The parent material from which soils in Southern Baldwin County were formed is composed of sediments deposited on beaches, flood plains and terraces as well as from geologic formations that crop out in the area (e.g., Citronelle formation and Hattiesburg clay) (McBride and Burgess 1964). In Southern Baldwin County, the relief is nearly level or gently sloping. This along with the type of parent material and the climatic conditions (e.g. long, warm summers, relatively short and mild winters, and high rainfall) favors the formation of permeable, well drained soils (Table 3) (McBride and Burgess 1964). Furthermore, the moderate warm temperature and high precipitation rates are not favorable to organic matter accumulation in these soils except where grass has been present continuously for many years (McBride and Burgess 1964). Accumulation of organic matter is of little importance in the formation of soil horizons (McBride and Burgess 1964).

The stratigraphy of Southern Baldwin County, as well as that of coastal and offshore Alabama, consists of a relatively thick Jurassic to Holocene sedimentary sequence (Chandler et al. 1985). At relatively shallow depths, interbedded sands, silts, gravels and clays comprise the middle Miocene to Holocene sedimentary rocks which hosts the freshwater aquifer zones of Baldwin County area. The thickness of these sediments regionally decreases towards the Gulf of Mexico. The aquifer system beneath Southern Baldwin County that serves as the source of freshwater is divided into three distinct units: the upper unit, known as the Beach Sand Aquifer or Aquifer Zone A1, is an unconfined aquifer consisting of white fine- to coarse-grained quartzose sands, silt, and locally sandy clay; the middle unit, known as the Gulf Shores Aquifer or Aquifer Zone A2, from confined to semi-confined to unconfined throughout the extent of the study area and is composed of coarse siliciclastic sand grains and gravel, and sporadic clay lenses; and the lower unit, known as the Deep Miocene Aquifer or Aquifer Zone A3, similar to Aquifer A2 in terms of lithology, with the exception that the sand and clay layers are more defined. Recharge to this aquifer zone occurs from

rainfall where the unit crops out, a few miles from the coast (Chandler et al. 1985). Therefore, under unconfined conditions, Aquifer Zone A2 is vulnerable to surface contamination for most of the study area. The three aquifers, developed as sources of fresh water for municipal, industrial, private and irrigation wells, have the ability to interact extensively in response to heavy, long-term pumping (Walter and Kidd 1979). A detailed description of the geology and hydrogeology of the study area is included in Murgulet and Tick (2007).



**Fig. 14** Distribution of major land-use/ land-cover classes (modified from Homer et al. 2004), isotope sample locations and identification number, and  $\delta^{15}\text{N}$  iso-contours for Southern Baldwin County, Alabama

In Southern Baldwin County, agriculture makes up a large percentage of the land-use/land-cover (Homer et al. 2004) (Fig. 14). Adjacent to the coastline, along the southern boundary (i.e. Gulf Shores, Orange Beach, and Perdido Beach), the developed LULC class is most pervasive and can be associated with recreational land uses (Fig. 14). High intensity developed areas are characteristic to the coastline and to a smaller extent to the inland study area.

Murgulet and Tick (2008) conducted an assessment study of the nitrate potential sources and contamination extent within the aquifer system of Southern Baldwin County using nitrate, chloride and land-use/land/cover data. The study indicates that in Southern Baldwin County, the nitrate contamination extends along several hot spots that are concentrated within areas of intense agricultural and residential land uses (Murgulet and Tick 2008). Results from Murgulet and Tick (2008) revealed very low nitrate levels in groundwater along the narrow coastal zones of the study area (along the Gulf of Mexico) within Aquifer Zone A1. Slightly increased nitrate concentrations in Aquifer A1 were identified to a small spatial extent in Fort Morgan Peninsula. Concentrations as high as 80.79 mg/L  $\text{NO}_3^-$  were observed in this aquifer. Analyses of deeper Aquifer Zone A3 indicate very low nitrate concentrations (Murgulet and Tick 2008). Chloride was observed to accompany some of the most elevated nitrate concentrations for each of the nitrate zones.

The present study takes a different approach for the nitrate source identification problem by implementing a novel analytical technique for quantifying nitrogen and oxygen stable isotopes of groundwater nitrate in conjunction with other geochemical data. In addition, this innovative method offers an unprecedented level of detail and information about the fate of nitrate in this groundwater system.

## Data and Methodology

To meet the objectives of this project nitrogen and oxygen stable isotopes of groundwater nitrate were used in conjunction with nitrate, chloride/bromide ratios (CL/Br), sulfate, and land-use/land cover data. This approach helps place constraints in nitrate fate and source identification by elucidating the impact of denitrification.

A number of sixty groundwater samples were collected from public supply, private, industrial, and irrigation groundwater wells analyzed for  $\text{NO}_3^-$ , phosphate, salinity, chloride, and total dissolved solids concentrations. Results of these analyses are presented in Murgulet and Tick 2008. Nitrogen and oxygen isotopes of groundwater  $\text{NO}_3^-$  (e.g.,  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$ ) were conducted for 34 of the groundwater samples. The spatial locations (i.e. longitude and latitude) of surveyed wells were recorded using GPS (Fig. 14). Groundwater samples were filtered, preserved, and analyzed within prescribed maximum holding times. The isotope data were used in conjunction with hydrogeochemical data to place constraints on potential sources of  $\text{NO}_3^-$ . These parameters were chosen because they are potential indicators of pollution from agricultural practices and (e.g., nitrate and chloride). Major elements were analyzed using a Dionex High Performance Ion Chromatograph (Model DX600, Dionex Corp., Sunnyvale, California) equipped with an autosampler, an anion-exchange column (7 mm; 4 x 250 mm; Dionex AS14A), and a conductivity detector (Dionex CD25), housed within the Geochemical Analytical Facility at the University of Alabama. The lower detection limit of the method was approximately 0.01 mg/L. Nitrogen and oxygen isotope of nitrate analyses were conducted at the Marine Microbial Biogeochemistry Lab, Woods Hole Oceanographic Institute using the Denitrifer Method (Sigman et al. 2001; Casciotti et al. 2002). To provide confidence in the sample analyses, the accuracy of the instrument, and therefore, to assure consistency of the results, triplicates of the anion and isotope analysis were conducted.

Land use practices are important factors that influence water quality and availability but their impact may be difficult to precisely determine on a regional scale. A landscape pattern is influenced by both natural processes and those generated by people. However in recent decades, human-generated processes have been the dominant force in determining the USA landscape pattern. Using the 2001 United States Geological Survey (USGS) Land Use/Land Cover (LULC) data (modified from Homer et al. 2004) the major LULC classes were identified. These type of data help delineate contaminant sources. The National Land Cover Database (2001) for mapping zone 46, produced by the Multi-Resolution Land Characteristics (MRLC) Consortium has been used to determine land-use/land-cover classes for Southern Baldwin County. The dataset was compiled from Landsat Thematic Mapper Plus (ETM+) satellite imagery (circa 2001) and it was supplemented by various ancillary data. Eight Level I LULC classes were identified for the area under investigation and are presented in Fig. 14. The LULC classification map depicted in Fig. 14 includes an explanation describing color schemes and class description. The assessments made from land-use/land-cover analysis are critical for identifying the location and origin of these nitrate sources to groundwater and surface water so that appropriate management and/or remediation strategies can be implemented proactively or in a timely manner.

Identifying sources and fate of nitrate in groundwater at a regional scale can be complicated and difficult to understand due to the mixing of nitrate from different sources and due to the extent to which denitrification occurs within an aquifer. Stable isotopes of nitrogen have been widely used as means of identifying nitrate sources. However, processes such as denitrification may complicate the source and fate identification process and may require additional investigations. The microbial denitrification of  $\text{NO}_3^-$  to  $\text{N}_2$ , preferentially utilizes  $^{14}\text{N}$  in the conversion to  $\text{N}_2$  causing an isotopic fractionation that leaves the remaining  $\text{NO}_3^-$

isotopically more enriched in  $^{15}\text{N}$ . This can make nitrate from partially denitrified fertilizer have the same  $^{15}\text{N}$  value as nitrate derived from animal waste. Therefore, for the purpose of this study, the newly developed technique of oxygen isotope ratio of nitrate ( $\delta^{18}\text{O}_{\text{NO}_3^-}$ ) was implemented in order to overcome limitations of the nitrogen isotope ratio alone. As with  $^{15}\text{N}$ , the  $^{18}\text{O}$  of the  $\text{NO}_3^-$  compound also becomes more enriched in  $^{18}\text{O}$  in the remaining  $\text{NO}_3^-$  during denitrification. In order to account for the mixing process, a two end-member mixing equation (modified from Faure and Mensing 2004) was implemented. Furthermore, sulfate concentrations were used in combination with the isotope data in order to either confirm or refute the presence of denitrification processes within the aquifer system.

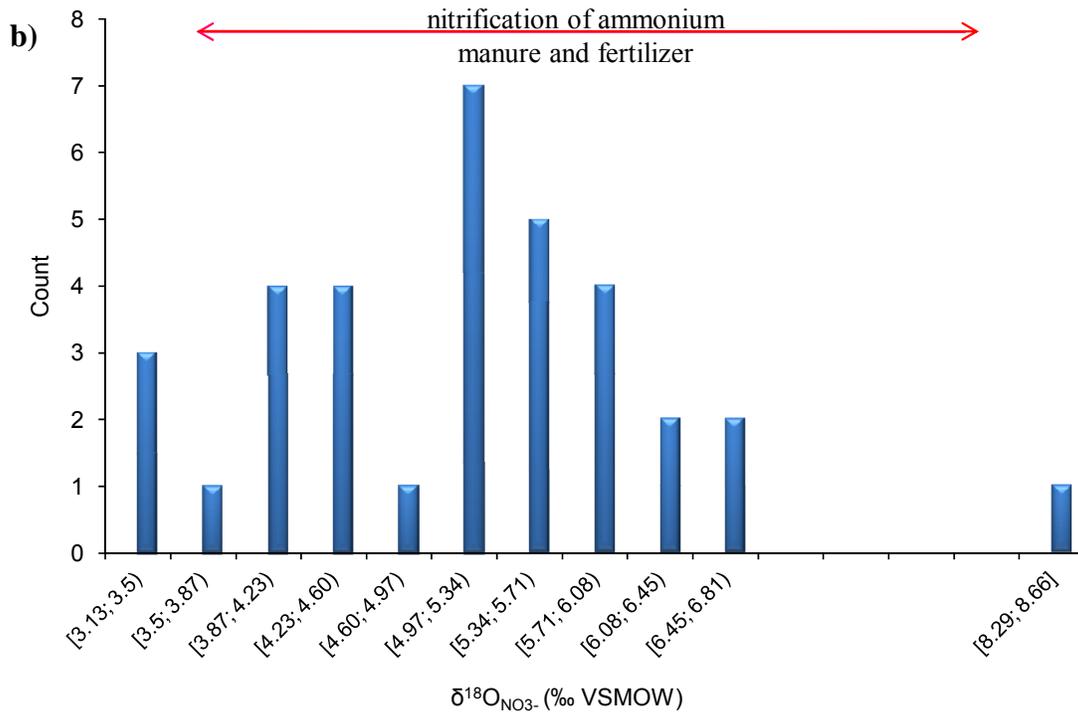
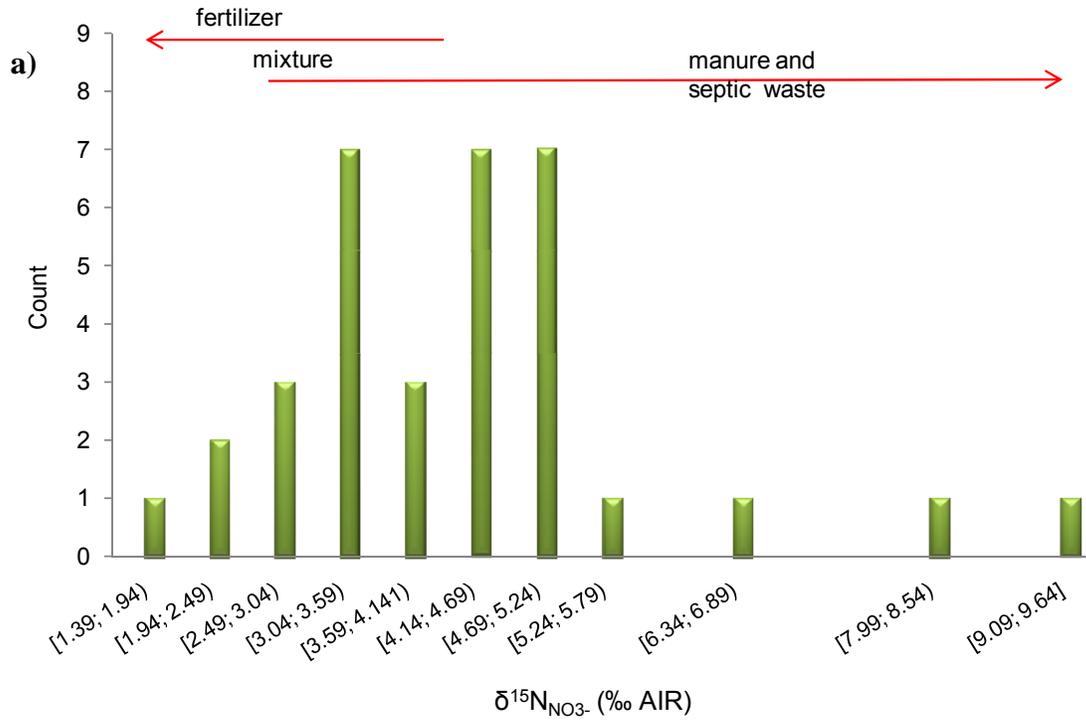
Chloride ( $\text{Cl}^-$ ) concentrations alone offer information on the salinity increase and possible contamination derived from multiple sources. However, when  $\text{Cl}^-$  concentrations are used in conjunction with bromide ( $\text{Br}^-$ ) concentrations (i.e.  $\text{Cl}^-/\text{Br}^-$  ratios), constraints can be narrowed allowing for the determination of specific types of salinity/contamination sources. For the purpose of this study, chloride/bromide ( $\text{Cl}^-/\text{Br}^-$ ) ratios were used to further aid in determining nitrate sources in groundwater. Chloride/bromide ratios were determined for groundwater samples investigated for nitrogen and oxygen isotopes of nitrate and were available for those samples that have bromide concentrations above the detection limit. The nitrogen and oxygen isotope data was compared to the  $\text{Cl}^-/\text{Br}^-$  ratios in order to place constraints on source identification. The classification criteria were based on the assumption that sources such as fertilizer would exhibit lower  $\text{Cl}^-/\text{Br}^-$  ratios and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values. Higher  $\text{Cl}^-/\text{Br}^-$  ratios and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values were attributed to sources such as sewer and manure. Furthermore, the  $\text{Cl}^-/\text{Br}^-$  ratio used in combination with the  $\delta^{15}\text{N}_{\text{NO}_3^-}$  data was used to identify nitrate sources in samples that may have been contaminated with saltwater (e.g. Murgulet and Tick 2007). Consequently,

$\delta^{18}\text{O}_{\text{NO}_3^-}$  values, sulfate, and the Cl/Br ratios were used to factor out the effects of denitrification when using  $^{15}\text{N}$  signature for nitrate source identification.

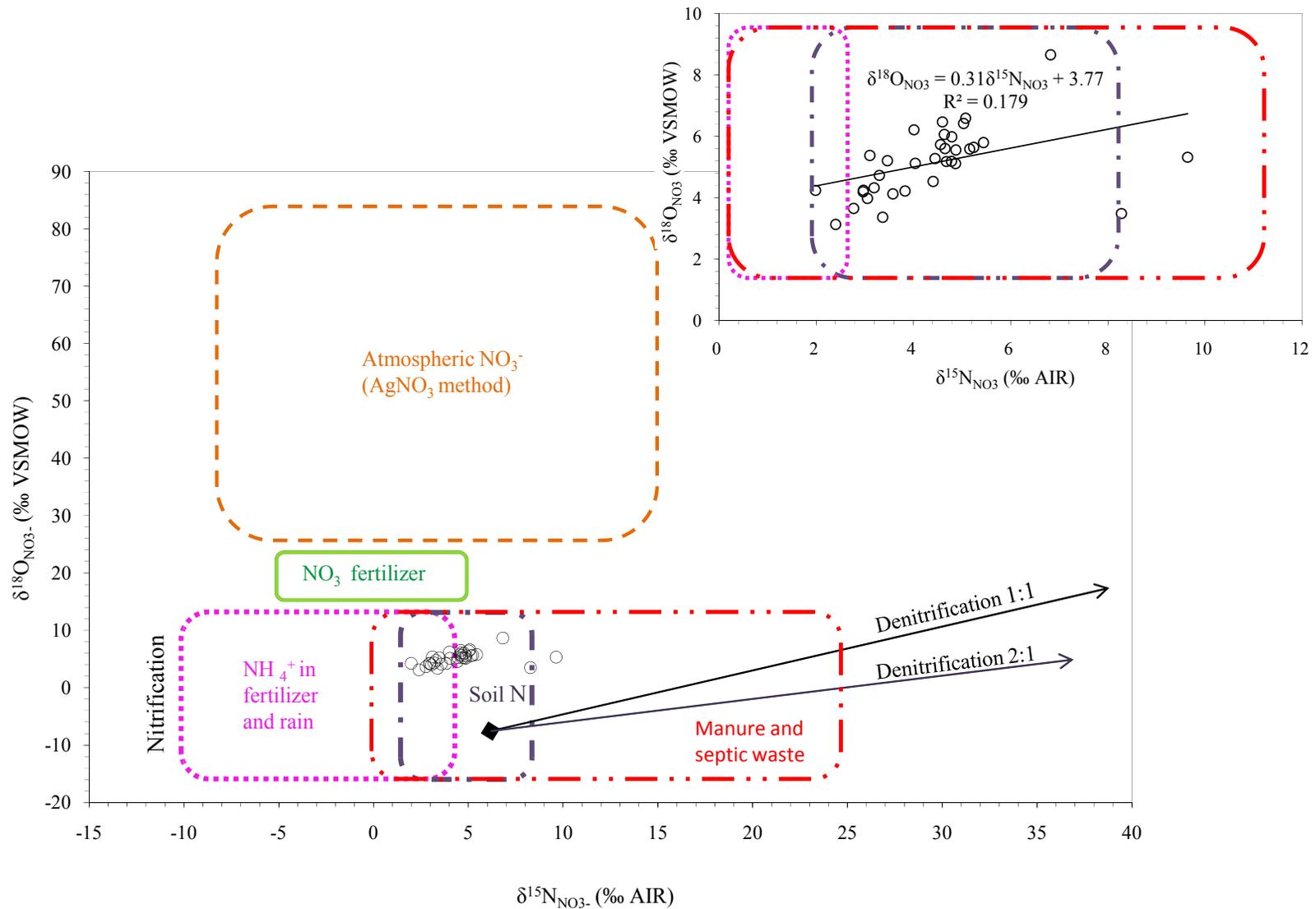
## Results

In Baldwin County LULC varies considerably (Fig. 14). The major classes of LULC that were identified were: water, developed, barrenland, natural forested upland, natural shrubland, herbaceous upland natural/semi-natural vegetation, herbaceous: pasture/hay, herbaceous: cultivated crops, and wetlands (Fig. 14). Based on the LULC classes distribution and frequency of occurrence within the study area it is most evident that agriculture (e.g. pasture/hay and cultivated crops) makes up the largest part of the study area. In Southern Baldwin County area, highly developed areas are not widespread. The majority of this region is characterized by medium-intensity development and open spaces which are primarily concentrated along coastal areas and in cities such as Daphne, Fairhope, Foley, and Gulf Shores (Figs. 13,14). Moreover, it is of most importance to recognize the rather dispersed distribution of residential areas (e.g. low intensity developed) within the agricultural fields (Fig. 14).

The  $\delta^{15}\text{N}$  of groundwater  $\text{NO}_3^-$  values ranged from +1.99 to +9.6‰ (Table 3). No groundwater samples had values within the commonly used range of fertilizers (Fig. 15a). Of the 34 samples, seven exhibited values of  $\delta^{15}\text{N}$  higher than +5 ‰ but only three were greater than +7‰ (Fig. 15a). The  $\delta^{18}\text{O}$  of groundwater  $\text{NO}_3^-$  data ranged between +3.12 and +8.7 ‰ (Fig. 15b). This narrow range of values plots within the field of  $\text{NO}_3^-$  derived from ammonium ( $\text{NH}_4^+$ ) nitrification from a combination of sources such as fertilizer, sewer, and manure (Fig. 16).

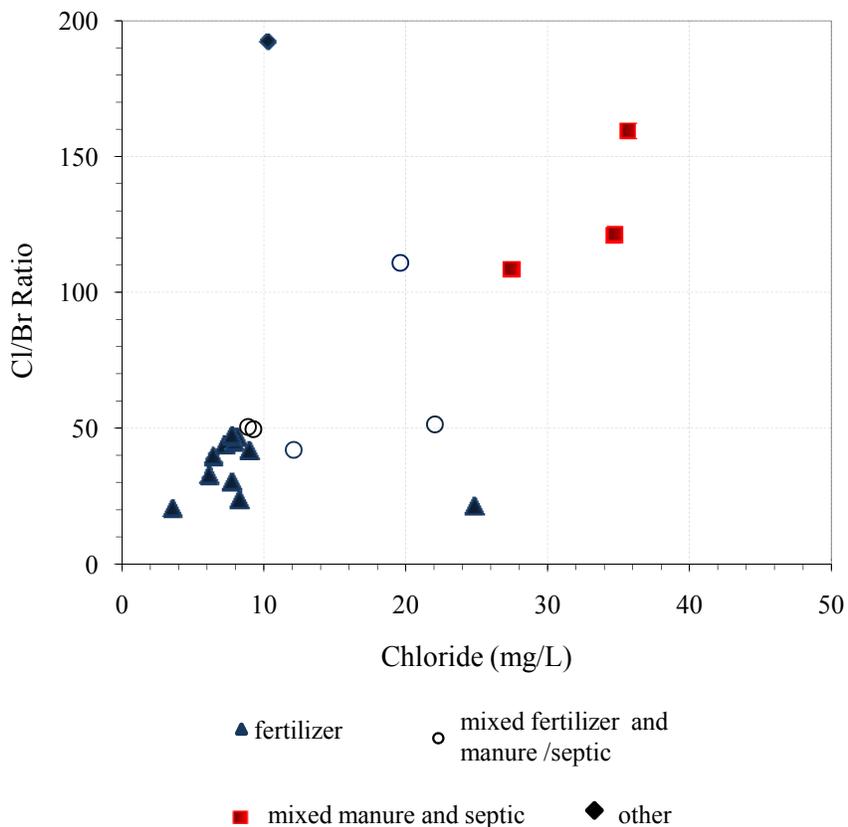


**Fig. 15** Histogram of  $\delta^{15}\text{N}$  (a) and  $\delta^{18}\text{O}$  (b) of groundwater nitrate and potential nitrate sources; arrows show potential  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  range of values for nitrate derived from nitrification of reduced N forms (Durka et al. 1994)

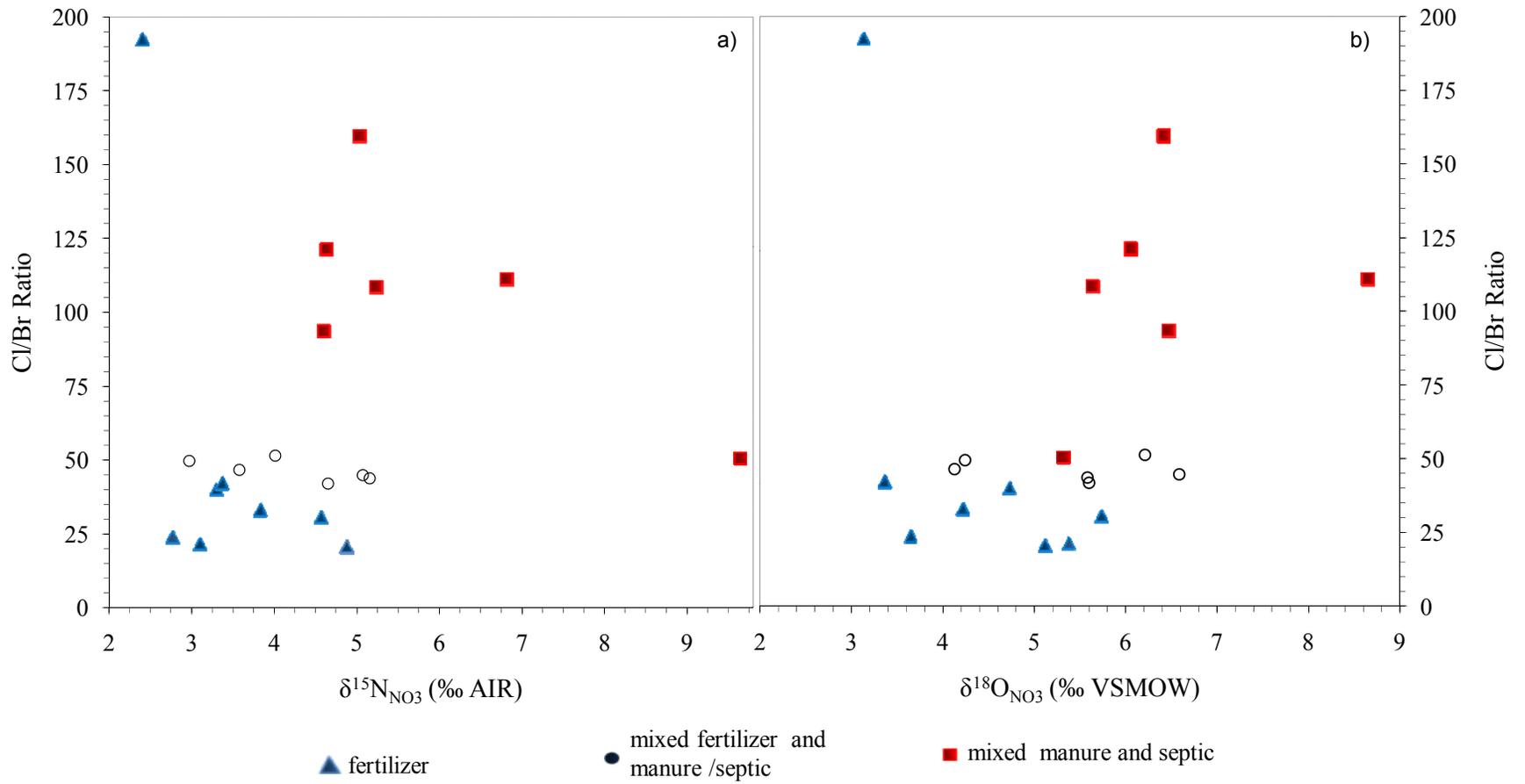


**Fig. 16** Ranges of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of nitrate from different sources (modified after Kendall et al. 2007). The insert represents a closer look of the  $\delta^{15}\text{N}_{\text{NO}_3^-}$  versus  $\delta^{18}\text{O}_{\text{NO}_3^-}$  crossplot for investigated groundwater samples

**Fig. 17** Relationships between  $\text{Cl}^-/\text{Br}^-$  ratio and chloride



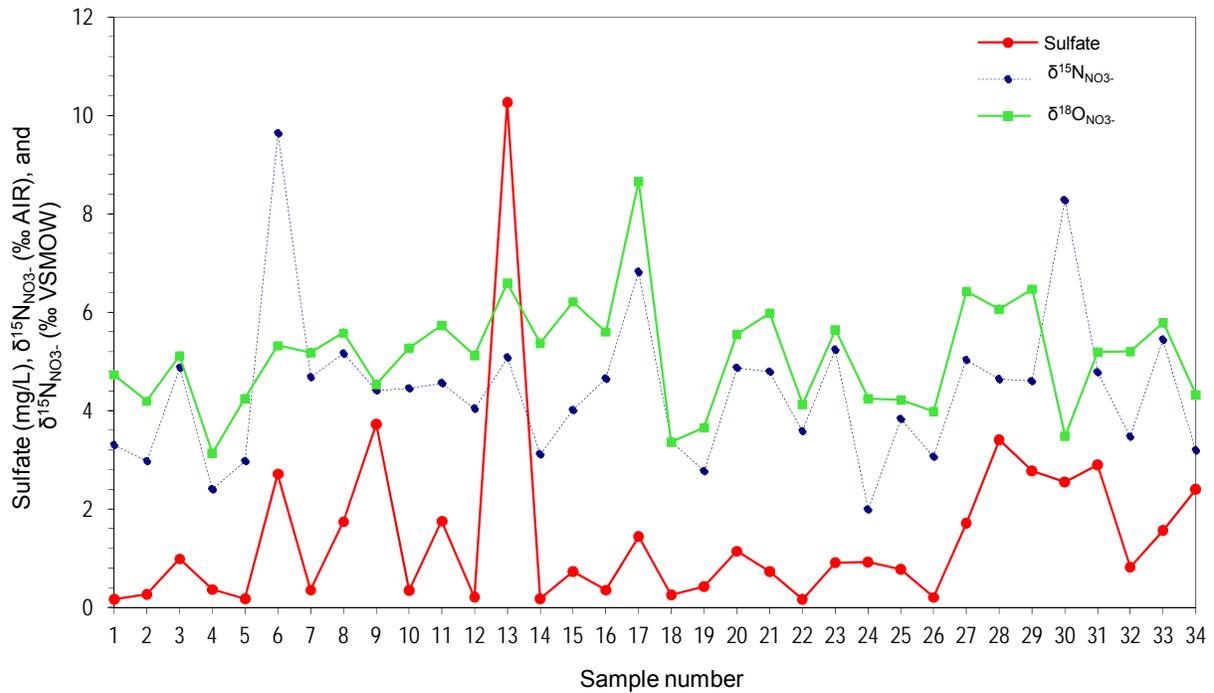
Chloride/bromide ratio values ranged from 20.47 to 192.34 (Table 3, Figs. 17, 18). Based on this range of values and the relationship with the chloride and isotope data, the nitrate sources could be placed into three groups: 1) mixed manure and septic; 2) mixed fertilizer and manure/septic; and 3) fertilizer (Table 3, Figs. 17, 18). Chloride/bromide ratios with values lower than 50 were most prevalent and indicate the predominance of fertilizer sources in the investigated groundwater study area. Higher  $\text{Cl}^-/\text{Br}^-$  ratios, associated with higher  $\text{Cl}^-$  concentrations were associated with groundwater impacted by saltwater contamination in close proximity to the Gulf of Mexico. This class (e.g. other) includes one sample and is depicted in Fig. 17. In this class could also be included two more samples located in areas contaminated with seawater, for which  $\text{Cl}^-/\text{Br}^-$  ratios were not available.



**Fig. 18** Source identification based on the relationship between: a) Cl/Br<sup>-</sup> ratios and  $\delta^{15}\text{N}_{\text{NO}_3}$  of groundwater nitrate and b) Cl/Br<sup>-</sup> ratios and  $\delta^{18}\text{O}_{\text{NO}_3}$  of groundwater nitrate

Table 3. Groundwater nitrogen and oxygen isotope, chloride, bromide, nitrate, sulfate, chloride-bromide ratios, fraction sewage and animal waste, and fraction fertilizer data

ID	Aquifer	$\delta^{15}\text{N}_{\text{NO}_3}$ . vs. atm. N2 (‰ AIR)	$\delta^{18}\text{O}_{\text{NO}_3}$ . vs. VSMOW (‰ VSMOW)	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Cl:Br	F <sub>sw</sub> (%)	F <sub>f</sub> (%)
1	A2	3.30	4.73	6.39	0.16	11.06	0.16	39.77	20.83	79.17
2	A2?	2.97	4.19	10.83	---	34.07	0.26	---	15.58	84.42
3	A2	4.87	5.11	3.51	0.17	1.22	0.98	20.47	45.79	54.21
4	A2	2.40	3.13	10.25	0.05	52.49	0.36	192.34	6.52	93.48
5	A2	2.97	4.24	9.26	0.19	22.61	0.17	49.65	15.58	84.42
6	A2	9.64	5.32	8.88	0.18	14.94	2.71	50.44	---	---
7	A3	4.68	5.18	4.57	---	3.23	0.35	---	42.77	57.23
8	A2	5.16	5.58	7.24	0.17	5.56	1.74	43.78	50.40	49.60
9	A2	4.41	4.53	4.72	---	3.28	3.72	---	38.47	61.53
10	A2	4.45	5.27	7.76	0.16	8.82	0.34	47.17	39.11	60.89
11	A2	4.56	5.73	7.71	0.25	12.78	1.75	30.32	40.86	59.14
12	A2	4.04	5.12	5.04	---	9.30	0.21	---	32.59	67.41
13	A2	5.08	6.59	7.91	0.18	5.96	10.27	44.94	49.13	50.87
14	A2	3.11	5.37	24.84	1.17	80.79	0.17	21.14	17.81	82.19
15	A2	4.01	6.21	22.06	0.43	53.40	0.73	51.45	32.11	67.89
16	A2	4.65	5.60	12.10	0.29	15.12	0.35	41.99	42.29	57.71
17	A2	6.82	8.66	19.63	0.18	5.50	1.44	110.91	76.79	23.21
18	A2	3.37	3.36	8.95	0.21	19.93	0.25	41.86	21.94	78.06
19	A2	2.77	3.65	8.23	0.35	15.16	0.42	23.49	12.40	87.60
20	A2	4.87	5.55	3.34	---	2.58	1.14	---	45.79	54.21
21	A2	4.79	5.98	3.41	---	1.46	0.73	---	44.52	55.48
22	A2	3.58	4.13	8.14	0.17	13.24	0.16	46.60	25.28	74.72
23	A2	5.24	5.64	27.45	0.25	47.19	0.91	108.44	51.67	48.33
24	A3	1.99	4.24	4.25	---	4.21	0.92	---	0.00	100.00
25	A2	3.83	4.22	6.11	0.19	12.78	0.77	32.83	29.25	70.75
26	A2?	3.06	3.98	12.56	---	54.39	0.20	---	17.01	82.99
27	A2	5.03	6.42	35.74	0.22	63.12	1.71	159.51	48.33	51.67
28	A2	4.64	6.06	34.76	0.29	55.31	3.41	121.24	42.13	57.87
29	A2	4.60	6.47	104.67	1.12	3.57	2.77	93.43	41.49	58.51
30	A1	8.28	3.48	43.96	---	11.27	2.55	---	100.00	0.00
31	A1	4.78	5.19	24.36	---	13.74	2.90	---	44.36	55.64
32	A2	3.47	5.20	4.55	---	2.37	0.82	---	23.53	76.47
33	A2	5.44	5.79	3.60	---	1.47	1.56	---	54.85	45.15
34	A2	3.19	4.32	2.44	---	0.87	2.40	---	19.08	80.92
Average	---	4.41	5.12	14.98	0.29	19.49	1.45	65.32	36.01	63.99



**Fig. 19** Sulfate concentrations and  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of groundwater nitrate relationships

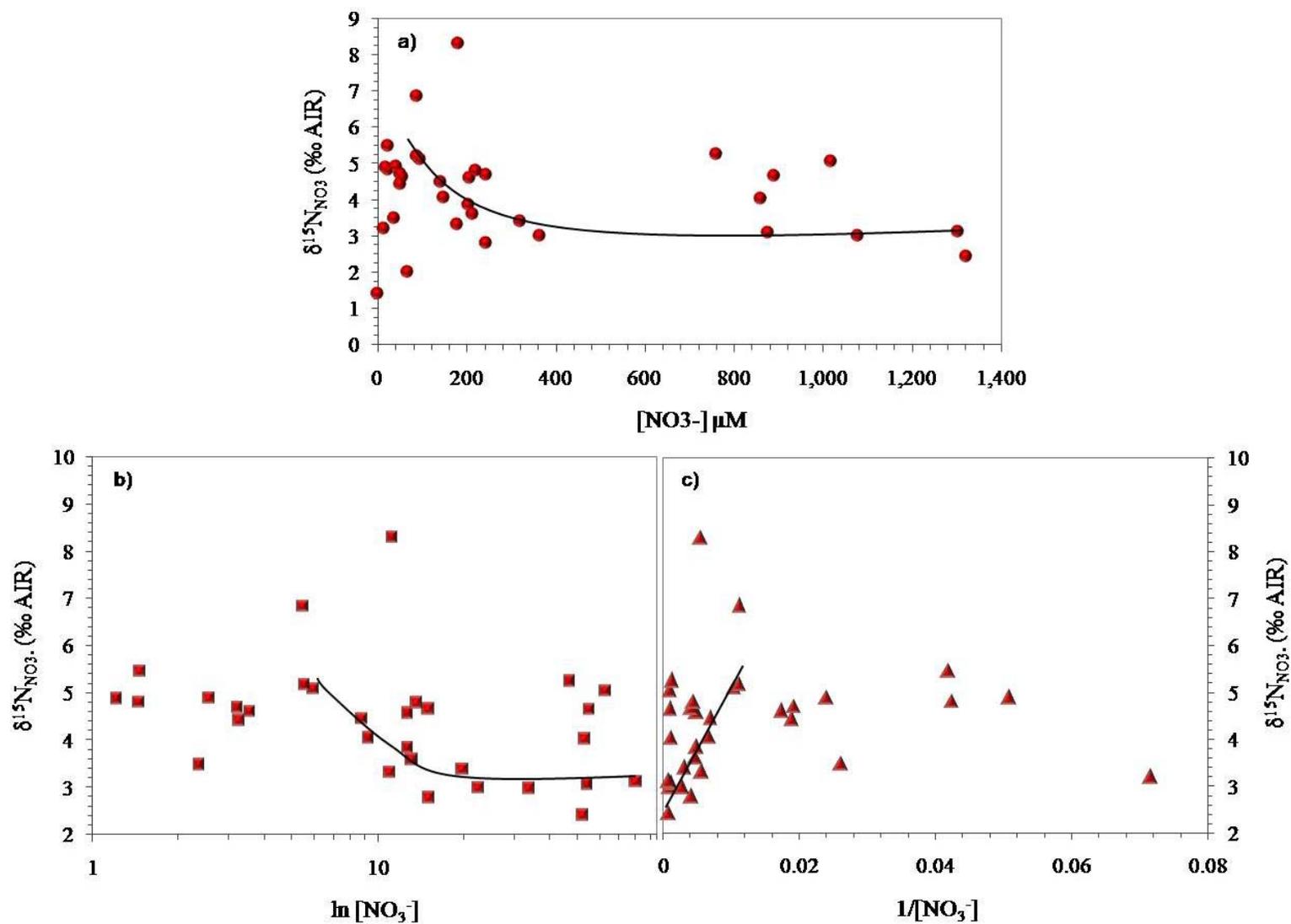
Fertilizer applications may contribute sulfate to groundwater. Even though sandy soils retain very little sulfur, most Alabama soils contain sufficient sulfate in the subsoil (Charles 1999). Nitrate and sulfate concentrations in groundwater are controlled by redox conditions in the aquifer. Sulfate concentrations in the investigated groundwater ranged from 0.16 to 10.3 mg/L (Table 3). However, concentrations lower than 4 mg/L were most pervasive and were associated with  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$  lower than +5 ‰ (AIR and VSMOW, respectively) (Fig. 19). The highest sulfate concentration (10.3 mg/L) was associated with a medium  $\delta^{15}\text{N}_{\text{NO}_3^-}$  value (5 ‰ AIR) and higher  $\delta^{18}\text{O}_{\text{NO}_3^-}$  value (+7.5 ‰ VSMOW) (Fig. 19) and with a fertilizer designated Cl<sup>-</sup>/Br<sup>-</sup> ratio of 44.94 (Table 3). However, given the frequency of sulfate concentrations, lower than 3 mg/L, the sample is classified as an outlier and can be ignored from

these analyses. Sulfate concentrations higher than 2 mg/L are coupled with  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$  values higher than 4 ‰ AIR and 4 ‰ VSMOW, respectively (Fig. 19).

### Discussion

Given the frequency of occurrence of the  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$  values (Figs. 15a, b) within the region, a major contribution of nitrate to groundwater can be attributed to fertilizer applications. Manure applications and sewer breakthrough appear to have a lower contribution to groundwater contamination. However, because of the higher frequency of the  $\delta^{15}\text{N}$  values above +2 (‰ AIR), the theory of mixing of groundwater fertilizer and sewer/manure end-members is plausible. The presence of alternative sources such as sewage and animal waste is also likely as the  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values are higher than the commonly recognized fertilizer  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values (Wassenaar 1995). Additionally, the presence of nitrate and chloride ions measured in groundwater at same locations supports the view that nitrate in groundwater may originate as well from manure sources. More than 90% have  $\delta^{15}\text{N}$  values lower than 6‰ (Fig. 15a). Furthermore, due to the sparse distribution of residential land uses (e.g., developed LULC class) (Fig. 14), leaching from septic tanks and animal waste to the saturated zone and mixing with ambient groundwater is possible and explained by the overlapping isotope signatures.

The  $\delta^{18}\text{O}$  of groundwater  $\text{NO}_3^-$  data ranged between +3.12 and +8.7 ‰ (Figs. 15b, 16; Table 3) with values evenly distributed throughout the aquifer units (Table 3). The range of values of this parameter is indicative of the fact that nitrate in groundwater has originated from nitrification of ammonium in soil from a mixture of sources such as those mentioned above.



**Fig. 20** Nitrogen-15 fractionation during denitrification: (a) plot of  $\delta^{15}\text{N}_{\text{NO}_3^-}$  vs.  $\text{NO}_3^-$ ; (b),  $\delta^{15}\text{N}_{\text{NO}_3^-}$  vs.  $\ln \text{NO}_3^-$ , and (c)  $\delta^{15}\text{N}_{\text{NO}_3^-}$  vs.  $1/\text{NO}_3^-$ . Mixing is suggested by nonlinear lines on graphs a) and b), and by a straight line on graph c) (e.g. Kendall et al. 2007)

The narrow ranges of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  ratios ( $\delta^{15}\text{N}$ : +1.99 - +9.6‰ and  $\delta^{18}\text{O}$ : +3.12 and +8.7 ‰) of the residual  $\text{NO}_3^-$  indicate that denitrification is not a predominant process in the surveyed aquifers. If denitrification was occurring, a distinct positive ratio shift would have been observed (i.e. approximately 2:1 or 1:1) for these two parameters (Böttcher et al. 1990; Kendall and McDonnell 1998).

The absence of denitrification is further supported by the relatively low  $\delta^{18}\text{O}$  values and the lack of inverse relationship between  $\text{NO}_3^-$  and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  (Fig. 20). Plots of  $\delta^{15}\text{N}$  versus  $\text{NO}_3^-$ ,  $\ln[\text{NO}_3^-]$ , and  $1/[\text{NO}_3^-]$  are presented in Fig. 20. These types of plots provide information about the presence of mixing end-members of sources with different N isotopic composition of residual  $\text{NO}_3^-$  and the extent to which denitrification has occurred. The plots depicted in Fig. 20 indicate that insignificant denitrification has readily occurred in these sandy aquifers. However, the data reveal mixing patterns evidenced by nonlinear lines  $\delta^{15}\text{N}_{\text{NO}_3^-}$  vs.  $\text{NO}_3^-$  and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  vs.  $\ln[\text{NO}_3^-]$  plots and by linear relationships between  $\delta^{15}\text{N}_{\text{NO}_3^-}$  vs.  $1/\text{NO}_3^-$  plots (Kendall and McDonnell 1998) (Fig. 20). Nevertheless, mixing patterns are very difficult to reconstruct given the scattered spatial location of the points.

In the aquifer system underlying Southern Baldwin County, nitrate, chloride, and sulfate are pervasive. The presence of these chemical species in groundwater is likely explained by the high frequency and distribution of agricultural sources.

In aquifers that receive nitrate contaminated waters, pyrite oxidation may occur resulting in enriched sulfate concentrations. In aquifers, the denitrification process has been coupled to sulfide (pyrite) oxidation (Schwientek et al. 2008). Under these conditions it is expected that decreasing nitrate concentrations will be coupled with increasing sulfate concentrations. Furthermore, groundwater nitrate should exhibit high  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$  values as a result of

denitrification (Fig. 19). Previous geologic analyses from this aquifer system have shown a direct lack of pyrite and sulfide bearing minerals (Walter and Kidd 1979). Therefore, the presence of sulfite and persistent elevated nitrate levels tend to indicate an oxygenated character of these aquifers whereby denitrification and sulfite reduction is less likely to occur. Furthermore, elevated sulfite concentrations associated with higher  $\delta^{15}\text{N}_{\text{NO}_3^-}$  cannot be explained by pyrite oxidation and nitrate conversion to nitrogen gas, but rather suggest the presence of sources such as fertilizer. Increases in  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$  values caused by denitrification are less likely in these highly conductive, coarse-grained and quartz-rich sandy aquifers, where water percolates rapidly and possesses higher dissolved oxygen concentrations than in finer-grained soils (Gormly and Spalding 1979).

#### Groundwater Mixing Estimation

In a groundwater system, where mixing of different end-member waters occurs, the resulting member does not preserve the original identity of the ambient groundwater. This water will have a new geochemical and isotopic characteristic which reflects, to varying extents, one or the other end-member characteristics. An estimation of the degree of mixing between two groundwater end-members can be done using a mixing equation like that from Faure and Mensing (2004). The degree to which sewage and/or animal waste and fertilizer were more likely to have influenced the groundwater signature in the study area was estimated using the modified equation from Faure and Mensing (2004). (e.g. equation 1).

$$\text{Equation. 1: } (F_{\text{sw}} \% * \delta^{15}\text{N}_{\text{sw}}) + (100 - F_{\text{sw}} \% ) * \delta^{15}\text{N}_{\text{f}} = (F_{\text{f}} \% + F_{\text{sw}} \% ) * \delta^{15}\text{N}_{\text{m}}.$$

Where,  $F_{\text{sw}} \%$  and  $F_{\text{f}} \%$  stand for the fraction sewage and animal waste and fraction fertilizer, respectively, in a particular sample. Furthermore,  $\delta^{15}\text{N}_{\text{sw}}$  and  $\delta^{15}\text{N}_{\text{f}}$  represent the  $\delta^{15}\text{N}$

values of sewage and animal waste and fertilizer, respectively (Table 3).  $\delta^{15}\text{N}_m$  is the measured isotope value of a particular groundwater sample.

For the mixing estimations, it was assumed that the lowest  $\delta^{15}\text{N}$  value measured in groundwater from below a field with a long history of agricultural practices where high pumping rates created high induced vertical flow rates is representative of the groundwater fertilizer end-member (e.g.,  $\delta^{15}\text{N}_f = 1.99 \text{ ‰ AIR}$ ). In addition, the highest  $\delta^{15}\text{N}$  value measured in a residential area isolated from agricultural fields that exhibited low  $\delta^{18}\text{O}$  values and  $\text{Br}^-$  concentrations below the detection limits, was assumed to be characteristic of the groundwater sewage and/or animal waste end-member (e.g.,  $\delta^{15}\text{N}_{sw} = 8.28 \text{ ‰ AIR}$ ). These values were used based on the presumptions that there was negligible mixing of different groundwater members at the selected locations and that  $\delta^{15}\text{N}_{\text{NO}_3^-}$  of nitrate in fertilized soils as well as of water collected directly from below sewage and/or manure contaminated fields may differ from that of groundwater sewage and/or manure and fertilizer.

The average percentage of fertilizer was estimated to be 64, whereas the average percentage of sewage and/or manure was 36. Mixing estimates suggest that fertilizer is the most prevalent source of nitrate in groundwater (Table 3).

### **Conclusions**

The results of this investigation provide a framework of the processes controlling nitrate transport in the aquifer system of Southern Baldwin County. Nitrogen and oxygen isotopes of groundwater  $\text{NO}_3^-$  were used in conjunction with land-use/land-cover and other hydrogeochemical data to place constraints on potential sources of  $\text{NO}_3^-$ . The  $\delta^{15}\text{N}_{\text{NO}_3^-}$  and  $\delta^{18}\text{O}_{\text{NO}_3^-}$  range of values suggests that nitrate is primarily derived from the nitrification of ammonium in soil from mixed sources such as fertilizer and manure and/or septic. Nevertheless,

given the higher frequency of samples with lower  $\text{Cl}^-/\text{Br}^-$  ratios and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values, the main source of  $\text{NO}_3^-$  in these aquifers can be attributed to agricultural practices. Moreover, estimations made using the mixing equation further indicate the predominance of fertilizer nitrate in the groundwater. Such observations coupled with the land use land cover distribution and aquifer hydraulics (e.g. mixing flowpaths) suggest that for most of the area, ambient groundwater is contaminated with  $\text{NO}_3^-$  originated predominately from agricultural practices and locally from alternative sources such as sewer breakthrough and manure application. Furthermore, the presence of sulfate from shallower to deeper parts of the aquifer system and the correlation of elevated  $\text{Cl}^-/\text{Br}^-$  ratios with the highest  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values allow concluding that denitrification was not an important process in these aquifers. Although denitrification may occur locally, mixing of different signature end-member waters makes it difficult if not impossible to resolve such processes under the large scale of the study. Therefore, it is expected that locally occurring denitrification will not have a significant impact on the overall nitrate removal. It is important to consider that in these highly conductive, oxygen-rich aquifers, where  $\text{NO}_3^-$  contamination is pervasive on recharge areas and denitrification is less likely to occur, nitrate concentrations are expected to increase and may adversely impact coastal discharge zones (i.e. wetlands, estuaries, lagoons, and coastal lakes) into the future.

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## CHARACTERIZATION OF THE GROUNDWATER FLOW SYSTEM OF SOUTHERN BALDWIN COUNTY, ALABAMA USING MULTI-ISOTOPE DATA

### **Abstract**

Southern Baldwin County Alabama has experienced continuously increasing growth and development over the last decade. Consequently, groundwater in the deeper aquifers in this area has been increasingly targeted for the region's growing municipal and industrial water needs. Expanding use of groundwater resources requires better knowledge about groundwater recharge and flow of the regional groundwater system. Therefore, assessment of the evolution of groundwater is necessary. The purpose of this study was to develop a better understanding of the regional flow system, with respect to recharge mechanisms and groundwater residence times of the aquifer system in Southern Baldwin County. Stable and radioactive isotope analyses of the aquifers in the region were implemented to assess primary recharge sources, groundwater ages and associated residence times, and evolution of groundwater along major flow paths. Groundwater samples from wells screened at different depths were analyzed for radioactive and stable isotopes such as Carbon-14 ( $^{14}\text{C}$ ) and carbon-13 ( $\delta^{13}\text{C}$ ), oxygen-18 ( $\delta^{18}\text{O}$ ) and hydrogen-2 ( $\delta\text{D}$ ), and oxygen and nitrogen isotopes of groundwater nitrate ( $\delta^{18}\text{O}_{\text{NO}_3}$  and  $\delta^{15}\text{N}_{\text{NO}_3}$ ), respectively. The  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\delta\text{D}$  isotope of groundwater data followed a relative narrow range regardless of aquifer depth. This narrow variation can be explained by modern environmental conditions and mixing processes. This is further supported by the  $^{14}\text{C}$  activities that indicate the occurrence of unexpected older groundwaters in the upper Aquifer A2, and younger groundwaters in the deeper parts of Aquifer A2 and Aquifer A3. The data further

suggest high vertical gradients and recharge likely due to the nature of the permeable sediments and potentially to increased gradients as a result of significant pumping. The lack of variation of  $\delta^{18}\text{O}$  values and the similarity to the regional precipitation  $\delta^{18}\text{O}$  data reflects primary mixing of different end-member waters, and the permanent input of local recharge waters to greater depths. Moreover, given the regional patterns of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\delta\text{D}$ , and  $^{14}\text{C}$  isotope data, the results of the study suggest that multiple recharge areas within this geographic area exist and are controlled by mixing during transport (due to naturally occurring and induced gradients), accounting for the groundwater homogeneous isotope signature. Furthermore, the  $\delta^{18}\text{O}_{\text{NO}_3}$  and  $\delta^{15}\text{N}_{\text{NO}_3}$  values reflect mixing processes that occur in a regional and highly developed groundwater system such as that of Southern Baldwin County. These isotope studies support the fact that the aquifer system in Southern Baldwin County is a highly dynamic system experiencing mixing of recent recharged waters with older, ambient groundwaters.

### **Introduction**

The over-development of the groundwater aquifers in Southern Baldwin County, Alabama for freshwater needs such as industry, agriculture, recreation and as drinking water supply poses a real concern for problems related to saltwater intrusion. Fresh groundwater resources in coastal Baldwin County occur in four principal aquifers. In order of decreasing depth these aquifers are: the Beach Sand Aquifer or Aquifer A1, the Gulf Shore Aquifer or Aquifer A2, and the 350-Foot Aquifer and the 500 Foot Aquifer or Aquifer A3. The upper two aquifers are heavily developed mainly for irrigation and water supplies purposes. Saltwater contamination was observed to have occurred in these upper two aquifers (e.g., Walter and Kidd 1979, Murgulet and Tick 2007). Furthermore, increased nitrate concentrations were identified in the Aquifer A2 Aquifer at shallow and greater depths (Murgulet and Tick 2008). Groundwater in

the confined aquifers of Southern Baldwin County has been increasingly targeted for the region's growing municipal and industrial water needs. Expanding use of groundwater resources requires better knowledge about groundwater recharge and flow dynamics of the regional groundwater system. In order to effectively manage the groundwater resources of the region a thorough understanding of the evolution of the groundwater is necessary. A comprehensive regional-scale study was conducted using a wealth of multi-isotopic data to develop a better understanding of the regional flow system, with respect to recharge mechanisms and groundwater residence times of the aquifer system underlying Southern Baldwin County, Alabama.

A comprehensive suite of isotopic tracers were used characterize the flow dynamics of the aquifer system. Groundwater samples from wells tapped at different depths were analyzed for radioactive and stable isotopes such as Carbon-14 ( $^{14}\text{C}$ ) and carbon-13 ( $\delta^{13}\text{C}$ ), oxygen 18 ( $\delta^{18}\text{O}$ ), hydrogen-2 ( $\delta\text{D}$ ), respectively. Isotope analyses were conducted because isotopes can be used as tracers of water movement and unique isotopic signatures are characteristic to particular recharge environments. These analyses provide vital measurements to constrain the period of time during which recharge occurred and identify the environment from which groundwater originated. The usefulness of these techniques have been proven by many researchers in the analyzes of a number of groundwater systems in the western U.S., including San Juan Basin, New Mexico (Phillips et al. 1989); Aravaipa Valley and Tucson Basin, Arizona (Adar and Neuman 1988; Campana and Simpson 1982); the Santa Clara Valley, California (Muir and Coplen 1981); and others.

Isotope measurements complement geochemical and hydrogeologic observations by providing identification of source waters and recharge rates (Stute et al. 1992; Ekwurzel et al. 1994). Isotopes are ideal tracers of groundwater sources and evolution along flow paths. Water

isotopes of hydrogen and oxygen (H and O) are best used in tracing sources of groundwater since they integrally compose the water molecule. Stable isotopes of hydrogen and oxygen provide us with information about recharge and discharge processes, and are effectively used in delineating recharge areas, in calculating mixing fractions between different end-member waters (e.g., different aquifers, different recharge sources, surface water and groundwater), as well as providing a timeframe of the geologic time when recharge likely occurred (Cook and Herczeg 1999). Carbon (C) occurs in all forms of organic life and is the basis of organic chemistry. The stable isotope carbon-13 ( $^{13}\text{C}$ ) is an excellent tracer of carbonate evolution in groundwater given its distinct range of values for different reservoirs. Overall,  $\delta^{13}\text{C}$  of groundwater DIC reflects the land-use/land-cover of the source area besides the water-rock interaction and any other additional geochemical reactions that may take place after the infiltrating water enters the saturated zone. Additionally, investigations of this parameter offer valuable information regarding age corrections when the radioactive isotope of carbon ( $^{14}\text{C}$ ) is used for groundwater dating.

In addition to the use of stable isotopes for groundwater source identification, ratios of conservative chemical elements such as bromide/chloride ( $\text{Br}^-/\text{Cl}^-$ ), iodide/chloride ( $\text{I}^-/\text{Cl}^-$ ), and fluoride/bromide ( $\text{F}^-/\text{Br}^-$ ) can as well be used because their ratios are characteristic and well defined for different types of waters (rainwater, seawater, sewage water, etc.) (Kazemi et al. 2006). These ions do not participate in chemical reactions along the groundwater flow paths under varying conditions. Thus, their concentrations are dependent on inputs from atmosphere, dissolution of materials, and the presence of different contaminants. Given the estimated concentration of each of these halogens within different contaminated waters and their conservative behavior, mass ratios can be successfully used to identify and locate contamination sources. Chloride is the most abundant ion of the halogens but present in low concentrations in

natural waters. Exceptions occur when a system receives inflow of water contaminated with seawater, sewage or industrial waste. While  $\text{Cl}^-$  concentrations alone offer information on the salinity increase,  $\text{Br}^-$  may indicate salinity sources. Thus, the ratio  $\text{Br}^-/\text{Cl}^-$  offers valuable information in groundwater investigations. Typical values for  $\text{Br}^-/\text{Cl}^-$  ratio in seawater are:  $3.47 \times 10^{-3}$  (mass ratio) or  $1.57 \times 10^{-3}$  (molar ratio) (Cook and Herczeg 1999). However, higher values have been observed (Cook and Herczeg 1999).

Non-conservative tracers such as nitrate can also be used in groundwater investigations and aquifer characterization studies. Nitrate concentrations in precipitation are generally small but variable reliant on source area and contamination impacts (e.g., human activities). Baseline concentrations of  $\text{NO}_3^-$ -N in groundwater are approximately 2 mg/L or below (Cook and Herczeg 1999). Groundwaters that exhibit concentrations above this limit are associated with anthropogenic pollution. The presence of this contaminant in groundwater at greater depths gives an indication of the recharge rates, the dynamics of the aquifer and information about the source area.

Typically freshwater originates primarily from precipitation, through infiltration from the surface through the soil and to the saturated zone. The radiocarbon isotope ( $^{14}\text{C}$ ) is one of the most widely used tools for age dating materials for many different applications. In particular,  $^{14}\text{C}$  has been extensively used for age dating groundwaters in the subsurface.  $^{14}\text{C}$  starts its journey from the atmosphere where it is dissolved in the rainwater. Measurements of  $^{14}\text{C}$  activity can be used to evaluate the “openness” of the system. Therefore, water with dissolved organic carbon (DIC) derived from soil will have a  $^{14}\text{C}$  activity similar to modern values.

In groundwater studies, the radioisotope  $^{14}\text{C}$  is used to estimate the time that a unit of water resides in the groundwater system. Most  $^{14}\text{C}$  in groundwater is introduced when recharge

water percolates through the soil zone. Measuring the relative abundance of the stable isotope  $^{13}\text{C}$  in groundwater provides another means of tracing carbonate evolution which is particularly useful for determining the importance of biogeochemical reactions in the groundwater system.

The purpose of this project is to characterize the local and regional flow system in the aquifers beneath Southern Baldwin County. The geochemical isotope analyses will help elucidate local and regional flow paths, groundwater ages and residence times through the groundwater system, recharge responses in the aquifers, and likely sources of groundwater in the region. This groundwater study can aid in the development of sustainable groundwater management strategies and improve risk assessments related to groundwater resource depletion and contaminant transport for the region.

### **Site Description and Background Information**

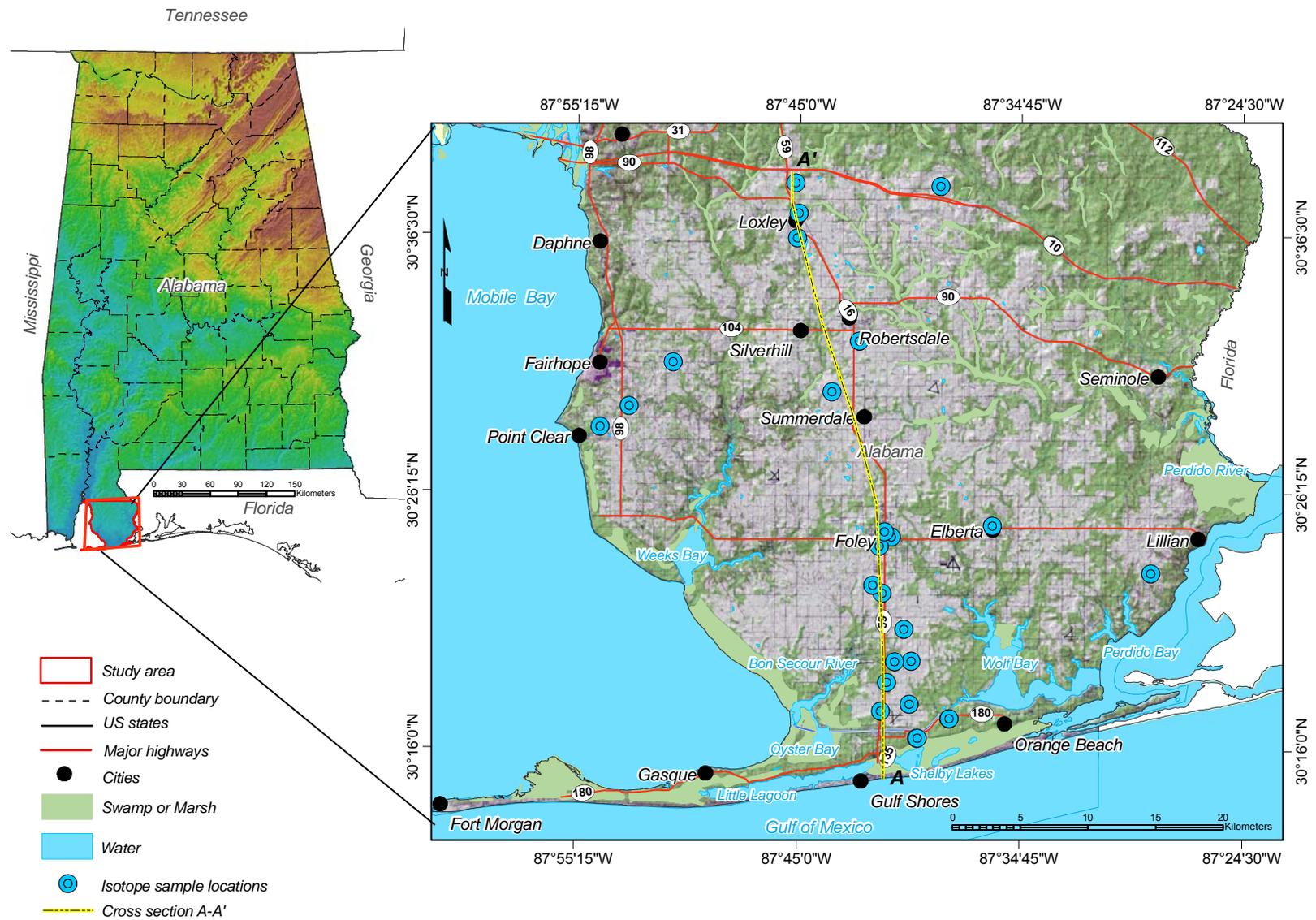
Baldwin County is one of the largest counties in Alabama. The research area comprises approximately 1,626 square kilometers ( $\text{km}^2$ ) in Southern Baldwin County. The study region is located South of Interstate 10 and is bounded by the Gulf of Mexico on South and by Mobile Bay, Perdido River and Perdido Bay on the West, Southeast and East, respectively (Fig. 21). Included in this study are areas vulnerable to saltwater contamination such as Fort Morgan Peninsula, Gulf Shores, Orange Beach and Perdido Beach (Fig. 21).

The population of Baldwin County increased significantly from 2000 to 2008 with the highest rates reported for Foley, Gulf Shores, and Fairhope (U.S. Census Bureau 2008). The economy of the county is based primarily on tourism, agriculture, fishery, and seafood processing industries. With these documented expansions of population and industrial development (i.e. cities and coastal areas), demands on water use in Southern Baldwin County have been observed to increase over the last few decades. Pumping rates in the region have been

observed to increase dramatically from 1980 until the most recent years (Chandler et al. 1985; Gillett et al. 2000).

Most of the study area is dominated by cultivated crops/agriculture and deciduous forest. Agriculture makes up a large percentage of the land-use within the study area (Murgulet and Tick 2009a). Recreational land uses account for a relatively high percentage of land-use along the southern boundary of the study area (i.e. Gulf Shores, Orange Beach, and Perdido Beach) (Murgulet and Tick 2009a). The highest intensity of development is generally located in areas which are in close proximity to the coastline (e.g., Gulf of Mexico and Mobile Bay) and some areas further inland with relatively higher population densities (e.g., Foley).

The physical features of Southern Baldwin County are representative of a typical coastal environment. The soil of this area is mostly sandy with high permeability. Therefore, precipitation infiltrates relatively fast, resulting in the absence of flowing streams. Under natural conditions, subsurface drainage follows the topographic relief. Precipitation in the southern part of Baldwin County averages approximately 165 cm per year (Kopaska-Merkel and Moore 2000). By and large, groundwater flows, from the sandy plateau, South to the lower marshlands, to the Intracoastal Waterway, Shelby Lakes, Little Lagoon, South-Southwest to Weeks Bay and Oyster Bay, and South-Southeast to Perdido River and Perdido Bay. Water from precipitation percolates to the water table becoming part of the aquifer system, flowing toward the discharge areas, where it intercepts the land surface, at a river/channel, lake, or bay.



**Fig. 21** Location of the study area and groundwater sample locations

During the summer and fall months, when precipitation is low and evapotranspiration rates are high, groundwater feeds surface waters and during the colder, wet months of spring and winter, groundwater replenishment takes place from direct infiltration or from surface water bodies.

The stratigraphy of Southern Baldwin County as well as that of coastal and offshore Alabama consists of relatively thick Jurassic to Holocene sedimentary rocks (Chandler et al. 1985). At relatively shallow depths, interbedded sands, silts, gravels and clays comprise the middle Miocene to Holocene sedimentary rocks which host the freshwater aquifer zones of Baldwin County area. The hydrologic system of Southern Baldwin County is a result of interactions between geological and physical environments, and water. The aquifer system beneath Southern Baldwin County is divided into three distinct units at the most southern portion of the study area: Aquifer Zone A1, Aquifer Zone A2 and Aquifer Zone A3. The unit is vertically separated into two units by clay of unknown continuity. These two units are the upper sand aquifer or Aquifer Zone A2(a) and the lower sand or Aquifer Zone A2(b). The marine clay separating Aquifers A1 and A2 pinches out to the North, hydraulically connecting the aquifers into one primary aquifer unit. However, the clay aquitards which exist in the southern part of Baldwin County pinch out northward at which point the aquifer system consists of two distinct units, Aquifer Zone A2 and Aquifer Zone A3, through the central portion of the study area. The clay layer separating the two aquifer units pinches out at depth beneath the city of Loxley (the northern boundary of the study area) at which point Aquifer Zones A2 and A3 become one large unconfined aquifer with intermittent confining lenses. However, it is important to point out that these intermittent clay lenses distributed throughout the aquifer system can produce semi-confined conditions. A hydrostratigraphic cross section of the study area is presented in Murgulet and Tick (2007).

Water predominantly enters the aquifer system of the study area predominantly from precipitation through infiltration and a very small amount comes from groundwater inflow (Walter and Kidd 1979). Water leaves the aquifer system by flow to surface waters, by evapotranspiration and groundwater outflow. A principal component of the water balance in this area is the groundwater outflow which has been increasing over the last decade or so due to increase groundwater use. As a result of increasing population, tourism, and development, groundwater pumping in the region increased from  $2.7 \times 10^7$  L/day to  $1.6 \times 10^8$  L/day between 1966 and 1995 (Reed and McCain 1971; Robinson et al. 1996a). Thus, downward infiltration from overlying aquifers may occur as result of overpumping or in the absence or intermittence of the confining layer. Precipitation is the main source of recharge within the Southern Baldwin County study area. Therefore, recharge is directly influenced by precipitation rates and infiltration rates. Precipitation is distributed among evapotranspiration (ET) and transpiration to the atmosphere, runoff to the local rivers and streams, and recharge to the local aquifers. Within the study area a relatively small part of precipitation enters the small rivers and streams. The minor rivers within the study region can only accommodate relatively small volumes of water from runoff.

In a recent recharge study, Dowling et al. (2004) reports that rainfall water may infiltrate as much as 40 to 60 meters into the local aquifers. As a result, it was determined that horizontal hydraulic gradients were very low and the vertical hydraulic gradients were relative high and mainly downward. The average recharge rates for the region were reported to be  $40 \pm 16$  cm/yr, and average discharge from Baldwin County to the Gulf of Mexico was reported to be  $1.9 \pm 0.8 \times 10^9$  m<sup>3</sup>/yr (Dowling et al. 2004). However, it is important to recognize that recharge and discharge rates are subject to dramatic fluctuation during periods of little to no rainfall and/or

during severe drought conditions affecting local groundwater conditions.

The most current studies in this region were conducted by Liu et al. (2007), Jin et al. (2008), and Murgulet and Tick (2007, 2008). The results presented by Liu et al. (2007) indicate that the area of Fort Morgan Peninsula exhibited extensive cones of water-table depression due to groundwater pumping and that this area is highly susceptible and vulnerable to saltwater intrusion. Jin et al. (2008) developed a numerical model and variable-density groundwater flow and predicted that further seawater intrusion into the coastal aquifers can occur as a result of increase groundwater use. Murgulet and Tick (2007) saltwater intrusion study indicates that groundwater quality in Southern Baldwin County is being degraded in the close proximity of the coast, due to elevated chloride concentrations. Furthermore, the recent study by Murgulet and Tick (2008) revealed considerable nitrate concentrations in some of the investigated private wells in Southern Baldwin County. Murgulet and Tick (2009a) conducted an isotope study for the identification of nitrate sources, mixing processes, and nitrate fate. The nitrate oxygen and nitrogen isotope data revealed mixing trends indicated by the mixing of end-members sources with different nitrogen-15 and oxygen-18 isotopic composition of residual nitrate and the absence of denitrification processes.

### **Methodology**

To fulfill the objectives of this study, isotope and geochemical investigations were conducted. Additionally, a classification of potential recharge areas was developed in order to reveal the openness of the system to modern water input.

A series of twenty six groundwater samples were collected from agricultural and municipal wells tapped at different depths in Aquifers A2 and A3 (Fig. 21). The samples were analyzed for stable isotopes of hydrogen, oxygen, and carbon as well as for dissolved inorganic

carbon (DIC) and radiocarbon ( $A^{14}C$ ) values. Before selecting water sample locations for source water investigation and groundwater dating, general flow paths were identified using the hydraulic gradients from Murgulet and Tick (2007). Using this information and based on the well log information availability, four hypothetical groundwater flow paths oriented North-West, north-Southeast and North-South were selected.

Groundwater samples were collected at the wellhead, from taps, after purging. Anion samples were collected in opaque amber (LDPE) bottles, filtered as soon as possible and stored in a refrigerator until analyzed. Isotope samples were collected in glass bottles with polyethylene caps to minimize the head space. Furthermore, isotope samples were treated in the field with mercuric chloride ( $HgCl_2$ ), in agreement with the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) standard preservation requirements for radiocarbon analyses and stored at room temperature in a dark environment until analyzed.

Stable isotope analyses and dissolved inorganic carbon (DIC) were conducted at the Alabama Stable Isotope Laboratory (ASIL) using the Finnigan Delta Plus GC isotope ratio mass spectrometer. Radiocarbon isotope analyses were conducted in two steps in order to defray the costs. The first step included the extraction of  $CO_2$  gas from groundwater samples using a gas extraction line housed at the ASIL, Geological Sciences. Through this process,  $CO_2$  dissolved in solution was transferred to a gas phase and trapped into a glass vial. In order to transfer the dissolved  $CO_2$  into the gas phase, water sample acidity was increased using anhydrous  $H_3PO_4$  acid. This process was repeated until all  $CO_2$  present in the water sample was transferred and trapped in the glass vial. Radiocarbon activity counting and age determination was conducted at the NOSAMS facility for the extracted  $CO_2$  gas samples. Radiocarbon ages are calculated based

on the radiocarbon half-life of 5,568 years and are reported without reservoir corrections or calibration to calendar years. The reported A<sup>14</sup>C activities are corrected to 1953.

Recharge area classification was developed using the 2004 United States Geological Survey (USGS) Land Use/Land Cover (LULC) and the STATSCO NRCS soil conductivity, runoff, and drainage layers. These layers were converted to grid files and reclassified accordingly using the ESRI ArcGIS computer program. For each of the four layers the reclassification was made based on the potential of a particular area to retain rainfall water and transmitted to depth. Thus, three classes were identified for each layer: class 0 (no retention water capacity), 1 (medium water retention capacity), and 2 (high water retention capacity). Recharge area classes were identified using the following equation:

$$RA=LULC*R*D*K_{sat},$$

Where: RA, R, D, and K<sub>sat</sub> stand for recharge area classes, runoff potential, soil drainage, and soil vertical conductivity, respectively.

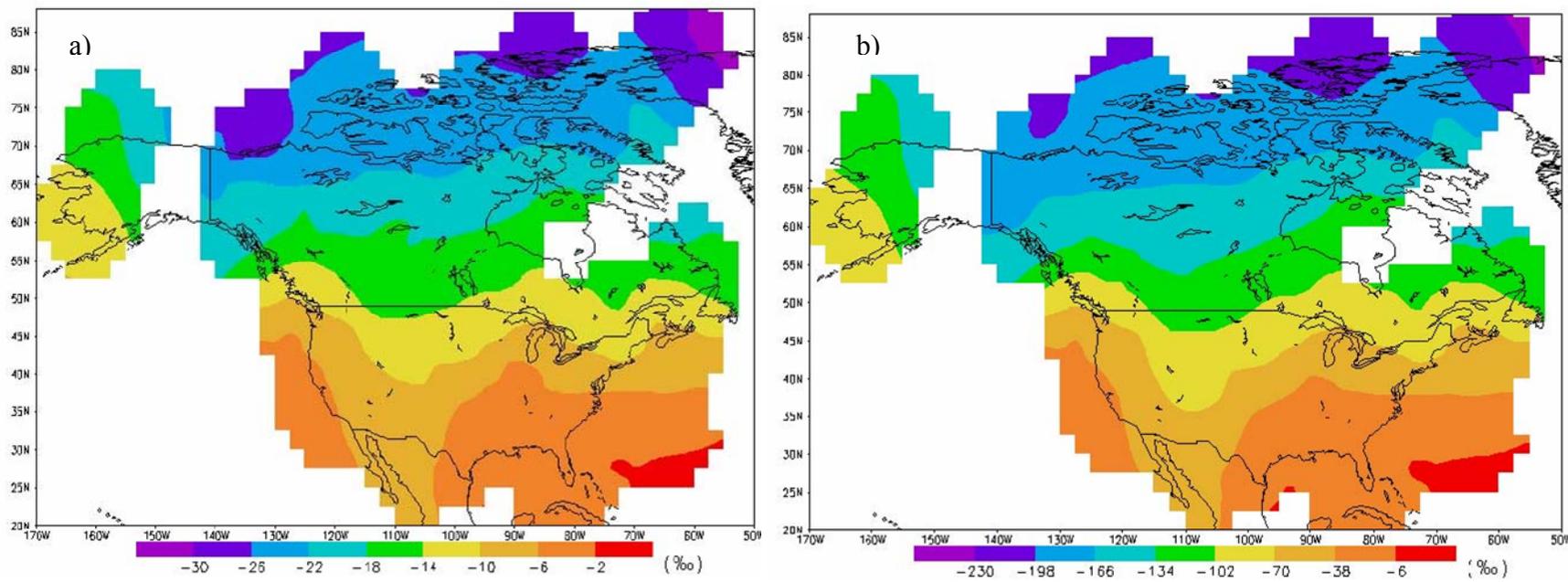
Major anion concentrations were measured using a Dionex High Performance Ion Chromatograph (Model DX600, Dionex Corp., Sunnyvale, California) equipped with an autosampler, an anion-exchange column (7 mm; 4 x 250 mm; Dionex AS14A), and a conductivity detector (Dionex CD25), housed within the Geochemical Analytical Facility at the University of Alabama. The lower detection limit of the method was approximately 0.01 mg/L. For ion chromatograph (IC) analyses, groundwater samples were first removed from the refrigerator allowed to equilibrate to room temperature and analyzed using a multi-point standard curve and diluted as necessary to remain within the linear range of the instrument. Triplicate runs were conducted to provide confidence in the sample analyses and instrument accuracy.

## Results

### Stable Isotopes of Oxygen ( $\delta^{18}\text{O}$ ) and Hydrogen ( $\delta\text{D}$ )

The hydrogen and oxygen stable isotopes have a predictable behavior during the hydrologic cycle of water from rainwater, runoff, evaporation, ice accumulation, and melting. The Global meteoric water line (GMWL) (Craig 1961a, b) reflects the isotopic evolution of waters going through these different processes. The GMWL is basically the average of a large number of local and regional meteoric waterlines and is defined by the following equation:  $\delta\text{D} = 8\delta^{18}\text{O} + 10 \text{‰ SMOW}$ . Hence, the position of water samples isotope signature with respect to the GMWL reveals the processes associated with the isotopic evolution of investigated waters.

Oxygen isotope values in groundwater from aquifers beneath Southern Baldwin County ranged from -3.5 to -4.4 ‰ (VSMOW) and had an average value of -4 ‰ (VSMOW) (Table 4). Hydrogen isotope values range between -16.2 to -21.7 ‰ (VSMOW) with an average value of 19.4‰ (Table 4). This type of water has similar oxygen and hydrogen isotopic signatures as precipitation water derived from maritime sources (e.g., Gulf of Mexico) that theoretically feed the study area's surface water and groundwater (Fig. 22). The mean distribution of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in precipitation data for North America from the International Atomic Energy Agency and World Meteorological Monitoring Program (IAEA WMO 2006), are depicted in Fig. 22 a, b). The minimum  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for Aquifer A2 are -4.25 and -21.73 ‰ VSMOW, respectively. The maximum  $\delta^{18}\text{O}$  and  $\delta\text{D}$  recorded for Aquifer A2 are -3.7 and -16.79 ‰ VSMOW, respectively (Fig. 23, Table 4).



**Fig. 22** Weighted annual  $\delta^{18}\text{O}$  (a) and  $\delta\text{D}$  (b) for North America (from IAEA/WMO (2006))

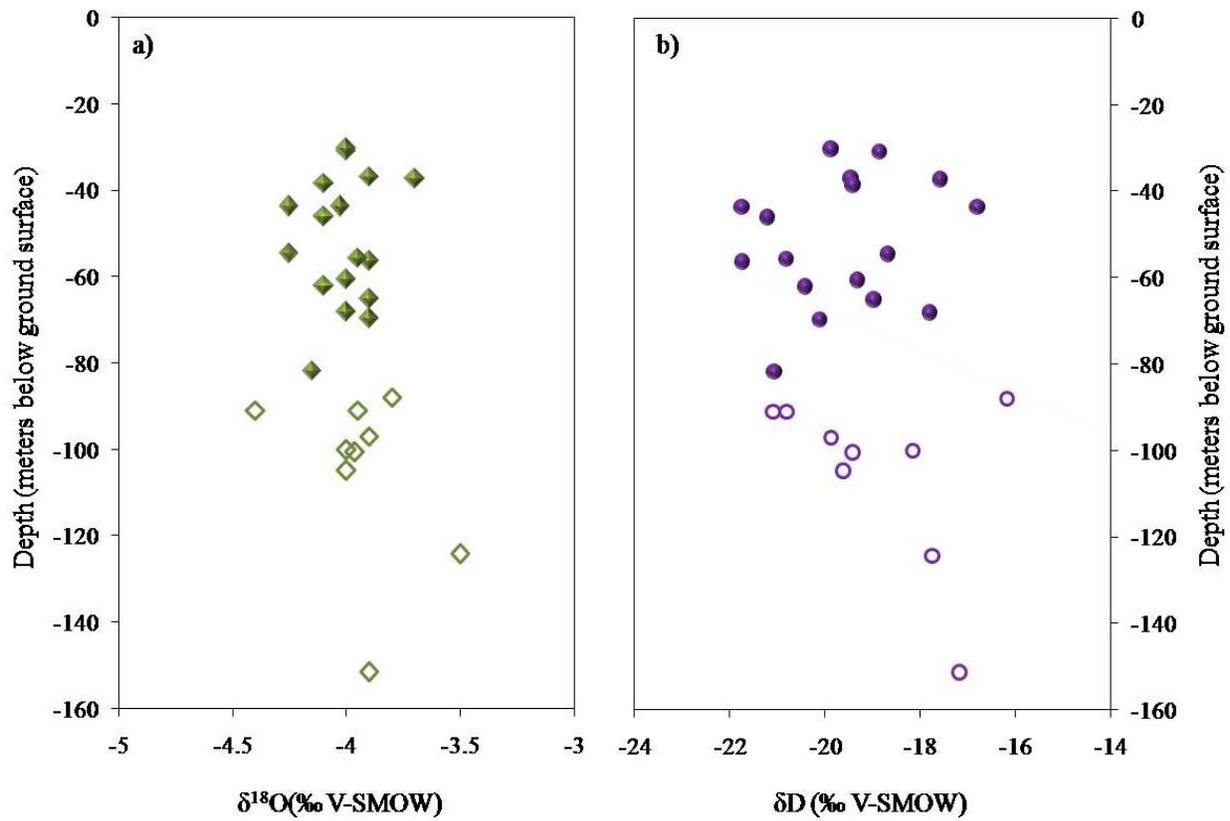
Table 4. Isotope analyses results and age estimation by aquifer

Well name	Aquifer	Depth (mbgs)	$\delta^{18}\text{O}$ (‰ VSMOW)	$\delta\text{D}$ (‰ VSMOW)	DIC (mM)	$\delta^{13}\text{C}$ (‰ VSMOW)	$\text{A}^{14}\text{C}$ (pmc)	Age	Age Error
Orange Beach (well#8)	A2&A3	101	-3.96	-19.41	0.81	-17.24	87.51	1,070	35
Gulf Shores (well#3)	A2	68	-4.00	-17.78	0.89	-16.53	68.56	3,030	20
Fairhope (well#2)	A2	82	-4.15	-21.05	0.53	-18.3	84.78	1,330	40
Loxley (well#2)	A2	55	-4.25	-18.67	0.28	-17.31	86.52	1,160	35
Robertsdale (well#4)	A2	37	-3.90	-19.45	0.67	-18.69	91.98	670	25
Gulf Shores (well#4)	A2	62	-4.10	-20.41	0.6	-16.62	92.31	640	20
Flowerwood Nursery (well#36)	A2	30	-4.00	-19.86	0.74	-18.35	97.60	195	30
Foley (well#10)	A2	61	-4.00	-19.31	0.68	-16.18	98.77	100	30
Orange Beach (well#2)	A2	38	-3.70	-17.57	1.30	-16.8	106.68	>Mod	-
Fairhope (well#4)	A2	70	-3.90	-20.10	0.76	-16.03	109.32	>Mod	-
Fairhope (well#9)	A2	56	-3.90	-21.72	0.68	-18.54	100.84	>Mod	-
Summerdale well	A2	56	-3.95	-20.79	1.03	-16.98	107.08	>Mod	-
Elberta well	A2	31	-4.00	-18.84	0.67	-18.64	104.72	>Mod	-
Orange Beach (well#1)	A2	44	-4.03	-16.79	0.81	-15.7	106.66	>Mod	-
Foley (well#11)	A2	38	-4.10	-19.40	1.12	-17.49	108.86	>Mod	-
Gulf State Park (shallow well)	A2	46	-4.10	-21.20	0.61	-18.68	104.48	>Mod	-
Loxley (well#1)	A2	44	-4.25	-21.73	0.27	-16.5	102.68	>Mod	-
<b>Average</b>	<b>A2</b>	<b>-</b>	<b>-4.02</b>	<b>-19.65</b>	<b>0.73</b>	<b>-17.33</b>	<b>97.61</b>	<b>-</b>	<b>-</b>

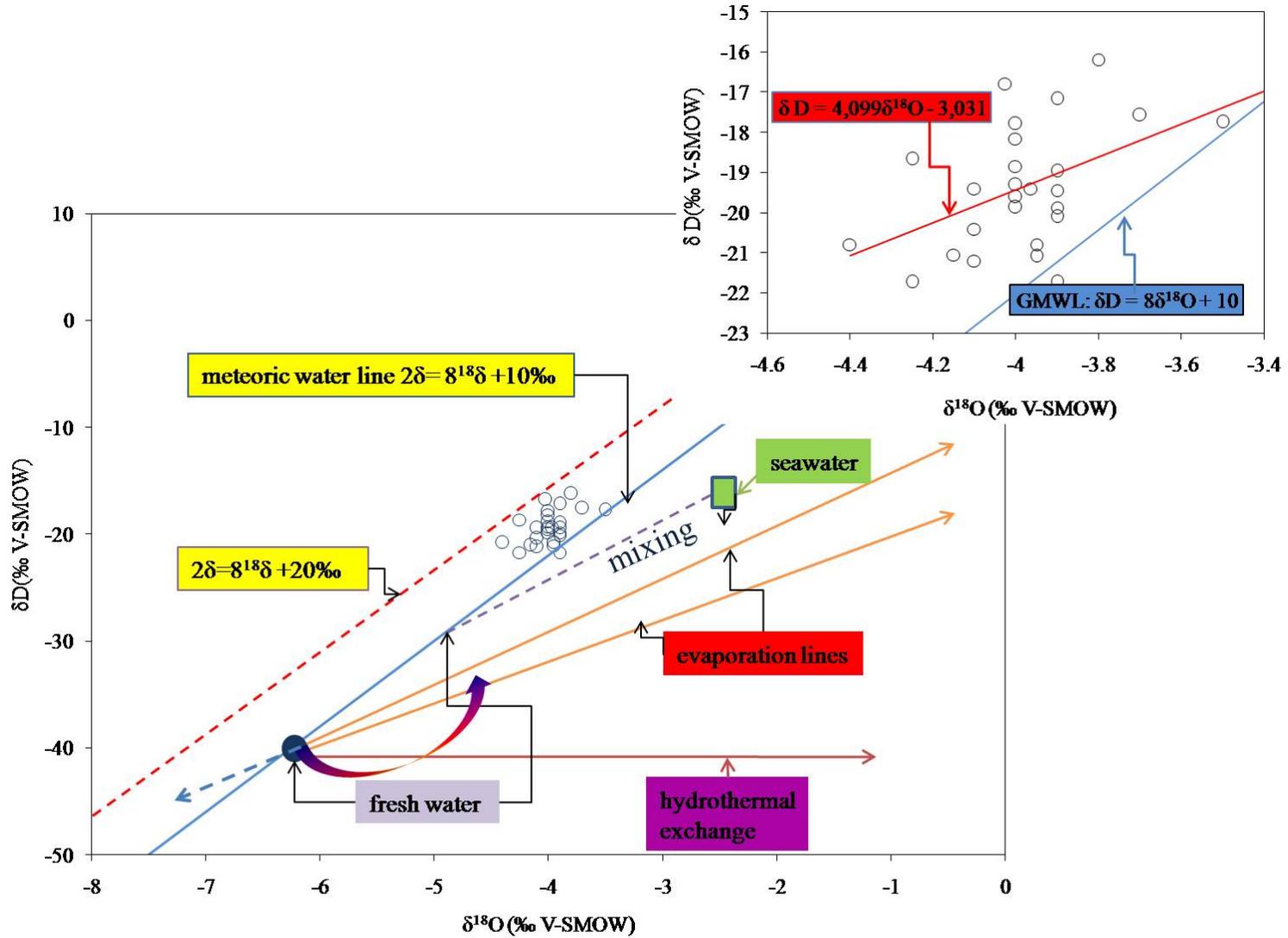
Table 4. Isotope analyses results and age estimation by aquifer contd.

Well name	Aquifer	Depth (mbgs)	$\delta^{18}\text{O}$ (‰ VSMOW)	$\delta\text{D}$ (‰ VSMOW)	DIC (mM)	$\delta^{13}\text{C}$ (‰ VSMOW)	$\text{A}^{14}\text{C}$ (pmc)	Age	Age Error
Gulf State Park (deep well)	A3	152	-3.90	-17.16	1.16	-15.55	38.81	7,600	25
Orange Beach (well#3)	A3	124	-3.50	-17.74	1.16	-13.48	50.31	5,520	25
Foley (well#12)	A3	65	-3.90	-18.96	0.60	-18.54	80.33	1,760	30
Perdido Bay (well # R25)	A3	91	-3.95	-21.08	0.60	-19.22	84.56	1,350	35
Fairhope (well#6)	A3	91	-4.40	-20.80	0.35	-17.86	87.24	1,100	30
Gulf Shores (well # 5)	A3	97	-3.90	-19.87	0.61	-17.25	88.38	990	30
Gulf Shores (well#9)	A3	100	-4.00	-18.16	0.84	-17.72	89.24	915	25
Foley (well#13)	A3	87	-3.80	-16.19	0.67	-17.65	92.53	625	30
Werner Turf Farm (Big Bertha well)	A3	104	-4.00	-19.60	0.59	-18.10	96.28	305	30
Orange Beach (well#8)	A2&A3	101	-3.96	-19.40	0.81	-17.24	87.51	1,070	35
<b>Average</b>	<b>A3</b>	<b>-</b>	<b>-3.93</b>	<b>-18.90</b>	<b>0.74</b>	<b>-17.26</b>	<b>79.52</b>	<b>2,123</b>	<b>29.5</b>

In Aquifer Zone A2, the average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotope values are -4.02 and -19.65 ‰ (VSMOW) respectively (Table 4). Aquifer Zone A3 exhibits similar range of values. The minimum  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for Aquifer A3 are -4.4 and -21.1 ‰ (VSMOW), respectively (Table 4). Samples collected from Aquifer Zone A3 exhibit maximum  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of -3.5 and -16.2 ‰ (VSMOW), respectively (Fig. 23, Table 4). The average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotope values for Aquifer A3 are -3.93 and -18.9 ‰ (VSMOW), respectively (Fig. 23, Table 4). Although the maximum  $\delta^{18}\text{O}$  value recorded for Aquifer A3 is higher than that of Aquifer A2, a single sample with this value was observed in one of the deepest wells and in closest proximity to the Gulf of Mexico and may represent the influence of seawater influx. Groundwater samples with the aforementioned range of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values were measured throughout the entire study area extending from the northern boundary (Interstate 10) to the Gulf of Mexico within both Aquifers A2 and A3 (Figs. 23, 24). Based on  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotope value distribution with depth, no preferential isotope signature was identified for different aquifers (Fig. 23). In addition, no correlations were observed between latitude and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values or between aquifer depth and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values (Figs. 23, 24).



**Fig. 23** Cross plot of  $\delta^{18}\text{O}$  (a) and  $\delta\text{D}$  (b) against depth below ground surface. Filled circles and diamonds represent the hydrogen and oxygen isotope data for Aquifer A2; Open circles and diamonds represent the hydrogen and oxygen isotope data for Aquifer Zone A3

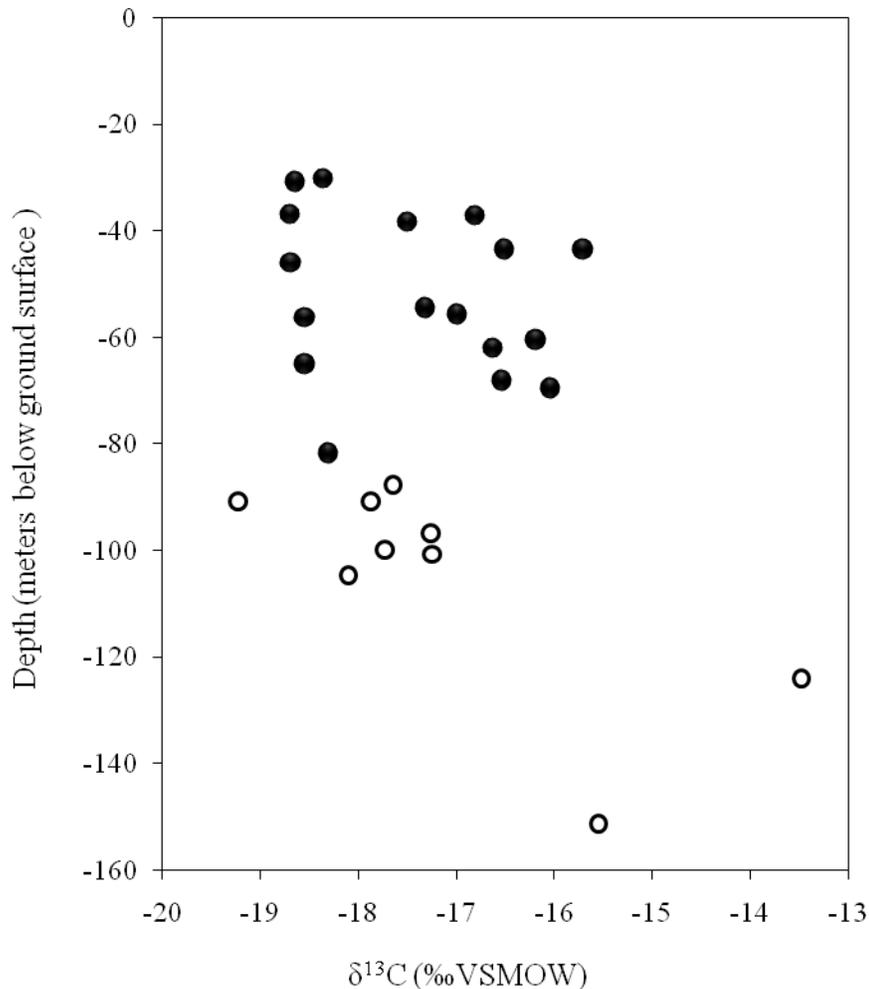


**Fig. 24** Hydrogen and oxygen isotope values plotted against the GMWL. The insert is a cross plot of hydrogen and oxygen isotopes and the local groundwater isotope line for Southern Baldwin County

## Stable Isotopes of Carbon ( $^{12}\text{C}$ and $^{13}\text{C}$ )

Carbon stable isotope analysis offers information about the type of groundwater and about the presence of water-rock interaction processes. When using radiocarbon as the dating tool, correct conclusions about the groundwater residence times are possible only when both  $\text{A}^{14}\text{C}$  and  $^{13}\text{C}$  concentrations are available and considered simultaneously (Polyakov and Seletsky 1979). The distinctive  $\delta^{13}\text{C}$  values for organic and inorganic carbon (-25 to -12 ‰ VSMOW for plants, -2 to +2 ‰ VSMOW for marine carbonates, and -12 to +2 ‰ VSMOW for soil carbonates) have been used to identify sources of DIC in groundwater (Deines et al. 1979). Unconfined, shallow aquifers have  $\delta^{13}\text{C}$  signatures very similar to those of pore-water and very similar to those of source waters. The  $\delta^{13}\text{C}$  signature of deeper, semiconfined and confined aquifers depends on the degree of vertical migration of groundwater, and the presence of geochemical processes within the aquifers. Therefore, mixing of different end-member waters is prevalent in many groundwater systems. Primary consideration should be attributed to the occurrence of this process when  $\delta^{13}\text{C}$  is used to identify sources of water. In the present case study, the range of values for  $\delta^{13}\text{C}$  is relatively narrow. The lowest  $\delta^{13}\text{C}$  value recorded in the study area was -19.22 ‰ (VSMOW) at a depth of approximately 100 meters in one of Perdido Water Utilities wells. The highest  $\delta^{13}\text{C}$  value of -13.48 ‰ (VSMOW) was measured at the southernmost well from a depth of approximately 125 meters in Orange Beach (Table 4). The deep Gulf State Park well (135 meters) and one of the shallower Orange Beach Water Utility wells (44 meters) exhibited relatively heavier  $\delta^{13}\text{C}$  values (e.g., -15.55 and -15.7 ‰ VSMOW, respectively) (Table 4). The average  $\delta^{13}\text{C}$  value of -17.31 ‰ (VSMOW) reflects the fact that the highest frequency of values falls under a more depleted range. Even though  $\delta^{13}\text{C}$  values are as high as -13.48 ‰ (VSMOW), it should be noted that only one water sample exhibited this value

(Fig. 25). Over the entire investigated area,  $\delta^{13}\text{C}$  values are nearly constant along the general North-South direction of groundwater flow. Moreover,  $\delta^{13}\text{C}$  values exhibited a similar range of value for both aquifers (Fig. 25). This indicates that geochemical reactions such as carbonate dissolution that could increase the DIC concentration are not significant.



**Fig. 25** Cross plot of  $\delta^{13}\text{C}$  values (‰ VSMOW) with depth (meters below ground surface). Filled circles represent the  $\delta^{13}\text{C}$  data for Aquifer A2; Empty circles represent the  $\delta^{13}\text{C}$  data for Aquifer Zone A3

The range of values for the investigated aquifers (-19.22 to -13.48 ‰ VSMOW) is characteristic of groundwater with DIC originating from inorganic sources such as plant root respiration (e.g., the Calvin or C3 cycle and the Hatch-Slack or C4 cycle). Measured  $\delta^{13}\text{C}$  of

groundwater are in the range expected in tropical and temperate environments with C4 plants (Mook 2006). However, in Southern Baldwin County in addition to the prevalent C4 plants, C3 type plants are also present. Therefore, it is expected that to some extent, the  $\delta^{13}\text{C}$  range of values is representative of two end-member groundwater mixing. The degree of mixing might be estimated using the published average carbon isotope values of the C4 and C3 type of plants (Vogel 1993).

### Groundwater Mixing Estimation

In a groundwater system, where mixing of different end-member waters occurs, the resulting member does not preserve the original identity of the ambient groundwater. This water will have a new geochemical and isotopic characteristic which reflects, to varying extents, one or the other end-member characteristics.

For this study the mixing degree between two groundwater end-members was estimated based on the  $\delta^{13}\text{C}$  signature for C3 and C4 plants using a mixing equation (equation 1) modified from Faure and Mensing (2004). The equation incorporates average  $\delta^{13}\text{C}$  values measured for C4 and C3 type of plants published by Vogel (1993). These values are -12.5 and -27.0 ‰ VSMOW, respectively. Furthermore, the measured  $\delta^{13}\text{C}$  value of each measured groundwater sample was incorporated into the equation.

$$\text{Equation 1: } (C4\% * \delta^{13}\text{C}_{C4}) + (100-C4\%)* \delta^{13}\text{C}_{C3} = (C3\%+C4\%)* \delta^{13}\text{C}_m$$

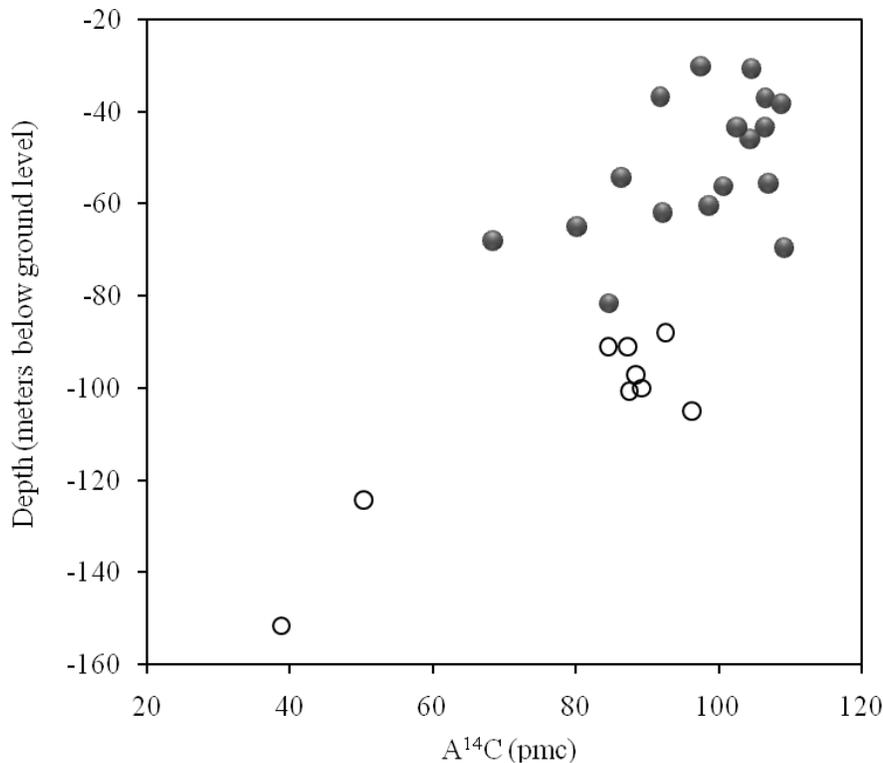
In equation 1, C4% and C3% stand for the percentage of C4 (e.g., Hatch-Slack cycle) and C3 (e.g., Calvin cycle) plants, respectively, in a particular sample.  $\delta^{13}\text{C}_{C4}$  and  $\delta^{13}\text{C}_{C3}$  represent the average  $\delta^{13}\text{C}$  values of the C4 and C3 plant cycles, respectively (Vogel, 1993).  $\delta^{13}\text{C}_m$  is the measured isotope value of the groundwater sample.

Minimum and maximum percentage range of C4 plants on groundwater samples was 54 and 93, respectively. The minimum and maximum percentage of C3 plants calculated were approximately 7 and 46, respectively. Generally, C4 plant isotopic signatures are the most prevalent in deeper groundwater. A very slight positive trend exists between C4 plant isotopic enrichment and depth. At shallower depths (e.g., approximately 30 m) the two end-members exhibit a similar percentage of influence on groundwater signature.

### Geochemical Tracers

Geochemical and radiocarbon results indicate that groundwater with lower  $A^{14}C$  concentration collected from Aquifer A3 has considerably less nitrate, chloride, salinity, and TDS concentrations compared to Aquifer A2. The highest nitrate concentrations were recorded in modern water samples collected from Aquifer A2 (47.20 mg/L  $NO_3^-$ ) (Murgulet and Tick [2009a](#)). This suggests that the nitrate contamination in Southern Baldwin County can be attributed to the post bomb (after 1953) development. Elevated chloride concentrations were identified in Aquifer A3 (17.24 mg/L) (Murgulet and Tick [2009a](#)), in waters collected from the southernmost and deeper sampled well (e.g. Gulf State Park deep well). The highest chloride concentrations were measured in the upper Aquifer A2 (104.67 mg/L), at the same location. The presence of nitrate and high  $A^{14}C$  concentrations in waters collected from the deeper Aquifer A2 and from Aquifer A3 reveal high permeabilities and relatively rapid flow dynamics (i.e. low residence times) within this aquifer system. In addition, the presence of nitrate at greater depths within the Aquifer system (i.e. A2 and A3) indicates the impacts of relatively recent anthropogenic activities/development and the high vulnerability of the aquifer system to contamination.

Groundwater in Southern Baldwin County has radiocarbon activities ( $A^{14}C$ ) ranging from 38.8 to 109 percent modern carbon (pmc) (Fig. 26, Table 4). These minimum and maximum values of  $A^{14}C$  were exhibited in groundwater samples from Aquifer A3 (deep Gulf State Park well) and from the upper Aquifer A2 (shallower Fairhope Water Utilities well), respectively (Table 4, Fig. 26). It should be noted that  $A^{14}C$  values are substantially higher at higher elevations within the aquifer reflecting the input of modern recharge waters from ground surface (Fig. 26).



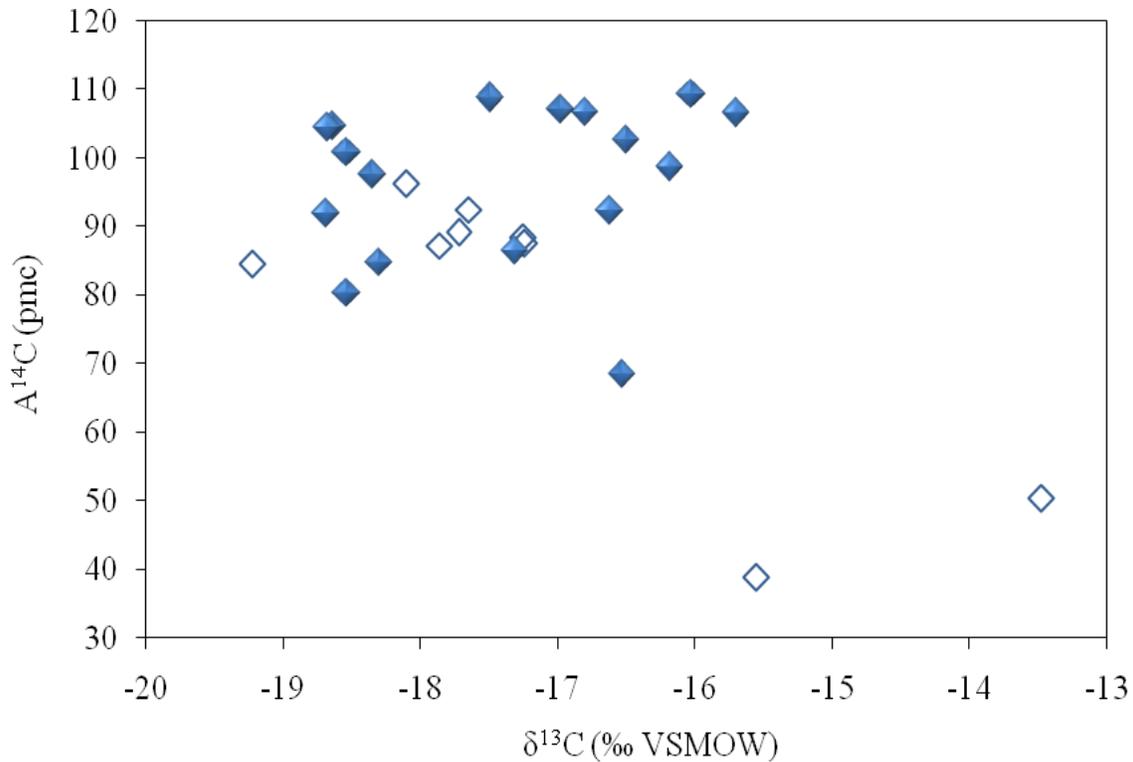
**Fig. 26** Relationship between radiocarbon concentrations (pmc) and depth in groundwater samples from Aquifers A2 (filled circles) and A3 (empty circles)

Most of the groundwater samples have  $^{14}C$  activities higher than 50 pmc with only two samples exhibiting values below 50 pmc (Fig. 26, Table 4). These two samples are collected from wells tapped in aquifer A3, in close proximity to the freshwater-seawater interface. Values

of  $A^{14}\text{C}$  above 100 pmc were measured in both upper and lower zones of Aquifer A2 (Fig. 26, Table 4).

The ratio  $^{13}\text{C}/^{12}\text{C}$  ( $\delta^{13}\text{C}$ ) is a reliable indicator of the evolution under open or closed system conditions of water in an aquifer system. Under open conditions, the carbon isotope ratio ( $\delta^{13}\text{C}$ ) is very similar to the average  $\delta^{13}\text{C}$  value of soil (-15‰ PDB – for Pee Dee Belemnite) (Deines et al., 1979). However, under closed conditions, the  $\delta^{13}\text{C}$  value of groundwater may become heavier as a result of water-rock interaction reactions (e.g., carbonate dissolution). Therefore, an increase in  $\delta^{13}\text{C}$  values associated with a decrease in  $A^{14}\text{C}$  concentrations would suggest an input of dead  $^{14}\text{C}$  derived from groundwater reactions with the aquifer matrix. The aquifer matrix in the study area is mainly composed of quartzitic sands. Hence, the carbon isotope signature of the groundwater in this aquifer system would not be influenced by mixing with  $^{14}\text{C}$  diluted groundwaters. A crossplot of the  $\delta^{13}\text{C}$  and  $A^{14}\text{C}$  values (Fig. 27) demonstrates this fact. In fact, a weak positive correlation between the two parameters can be observed (Fig. 27).

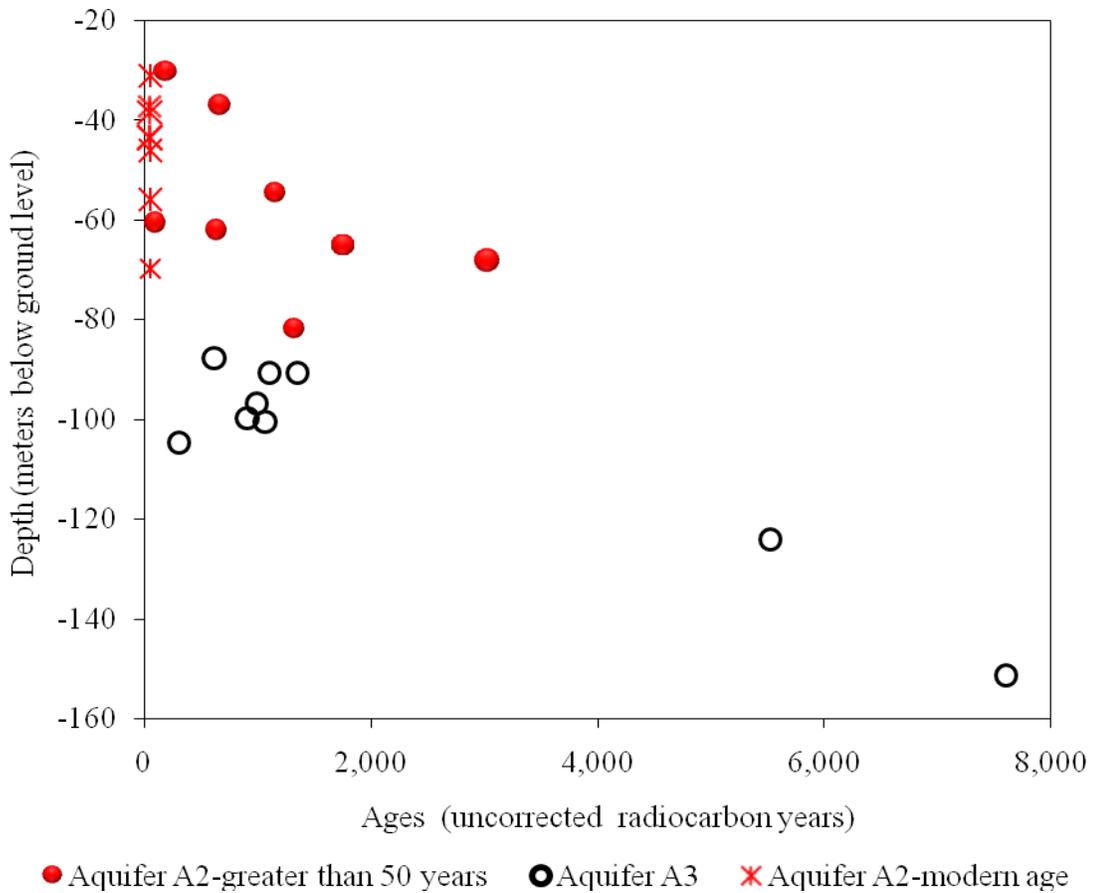
However, two groundwater samples collected from wells tapped in the coastal Aquifer A3 (e.g., the deep Gulf State Park and one of the Orange Beach Water Utilities wells), exhibit a different behavior. At these two locations, the smallest  $A^{14}\text{C}$  (e.g., 38.8 and 50.3 pmc, respectively) and the heaviest  $\delta^{13}\text{C}$  (e.g., -15.55 and -13.48 ‰ VSMOW, respectively) values were measured (Fig. 27).



**Fig. 27** Relationship between  $\delta^{13}\text{C}$  composition and  $A^{14}\text{C}$  concentrations in groundwater samples from Aquifers A2 (filled diamonds) and A3 (empty diamonds)

### Relative Groundwater Ages

In Southern Baldwin County, uncorrected radiocarbon ages of groundwater range from modern (recharged after 1960) to thousands (i.e. 7,600) of years. Most of the modern waters are present in the top part of Aquifer A2. However, modern waters were identified as well as deep as 70 meters in Aquifer A2 (Figs. 28, 30). There are also isolated cases of older groundwater measured within Aquifer A2 at relatively shallower depths (Figs. 28, 30). These particular samples were located in the northern site of the study area, in Loxley (Fig. 21). Furthermore, groundwater ages in the order of thousands of years (e.g., radiocarbon years) occur only in a few samples. The oldest uncorrected radiocarbon age was exhibited at the southernmost well, screened in Aquifer A3 at approximately 152 meters below ground surface (Figs. 28, 30).

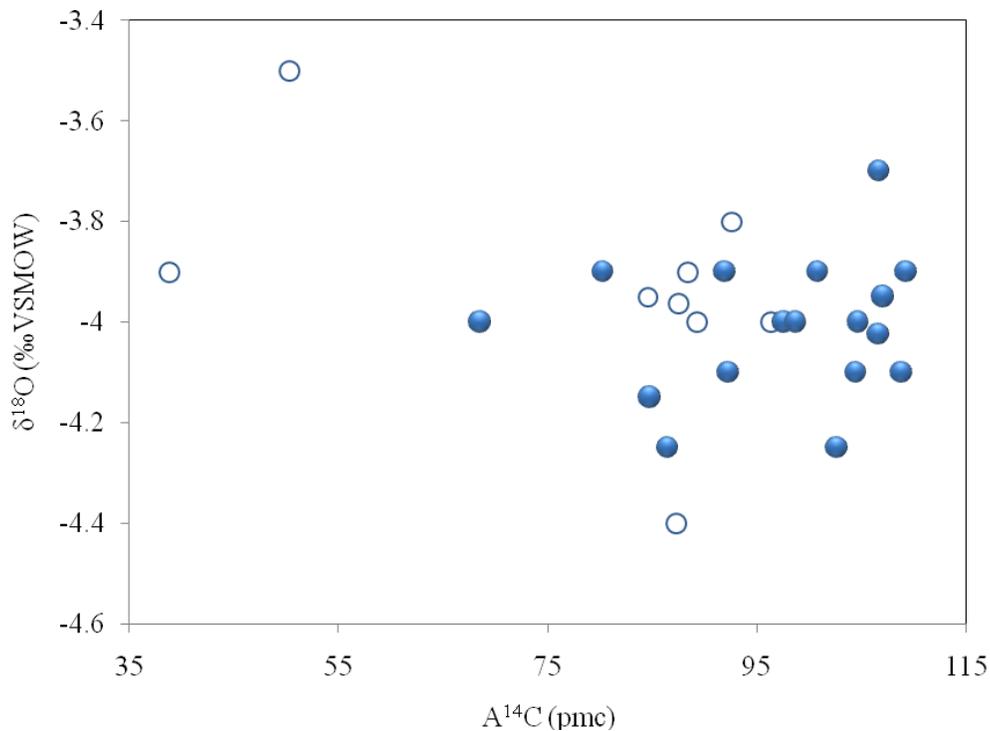


**Fig. 28** Relationship between groundwater radiocarbon ages and depth in groundwater samples from Aquifers A2 and A3

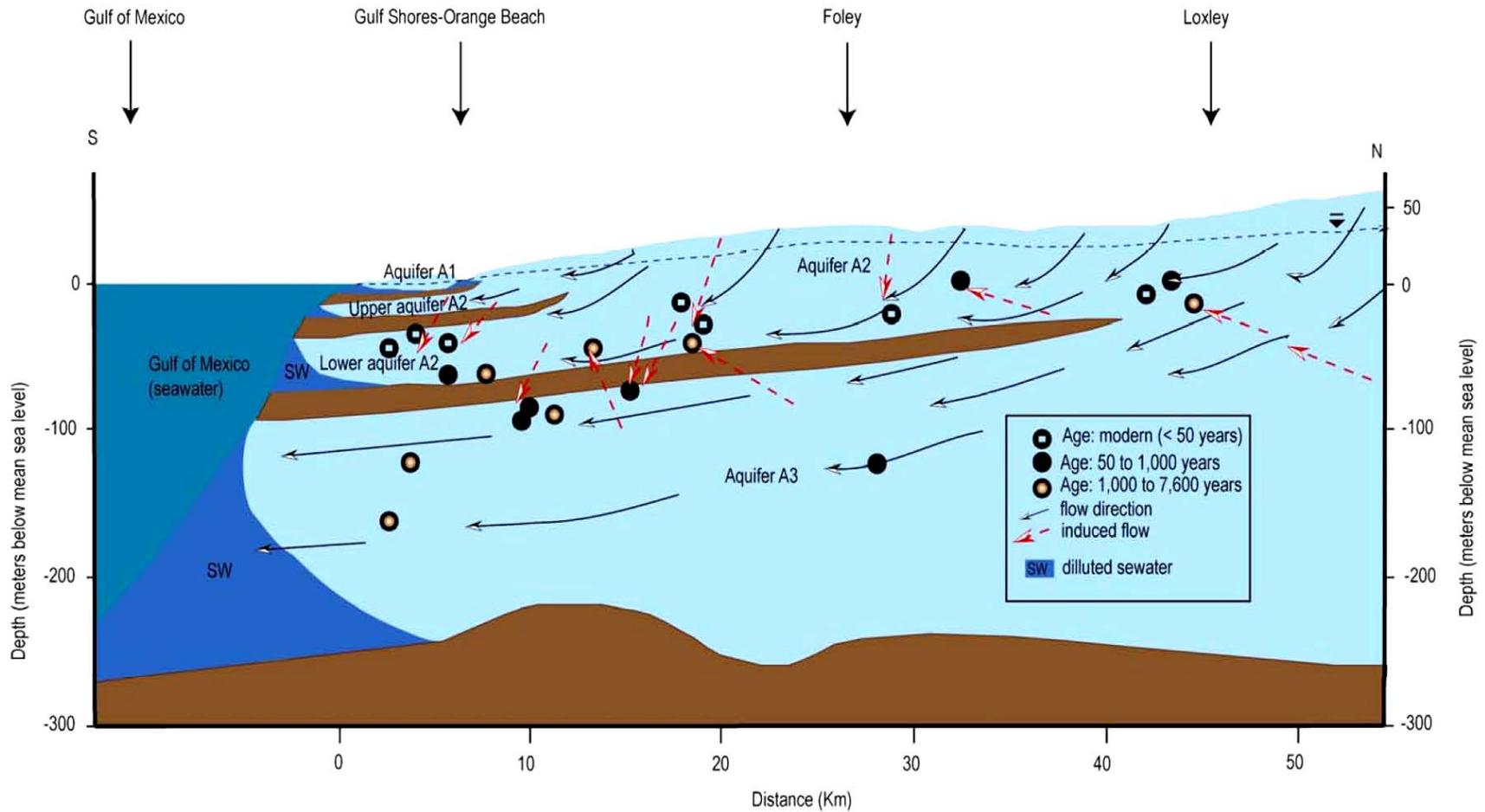
The range of carbon isotope data for the investigated aquifers indicates that there is no  $^{14}\text{C}$  enrichment between aquifer matrix and groundwater DIC. This is further supported by the aquifer matrix composition (e.g., mainly quartzitic sand and gravel). Therefore, in the investigated groundwater system,  $^{14}\text{C}$  activity may be apportioned between exchange with  $\text{CO}_2$  in the soil and groundwaters of different  $^{14}\text{C}$  activity. Moreover, calculated groundwater ages need no corrections for water-rock interaction reactions. However, mixing of fresh groundwater with seawater would increase  $\delta^{13}\text{C}$  and DIC values of groundwater and consequently,  $A^{14}\text{C}$  would decrease and resulting groundwater ages would be exaggerated. Given the oxygen-18, hydrogen-2, and carbon-13 values and the location relative to the freshwater/seawater interface, samples

collected from the deeper and shallow Gulf State Park wells and from Orange Beach municipal well 2 may have been attributed overestimated ages as a result of  $^{14}\text{C}$  input from seawater (Figs. 26, 30).

The  $\delta^{18}\text{O}$  data do not show a southerly interbasin flow. Moreover, the  $^{14}\text{C}$  concentrations do not consistently decrease along flow paths and with depth as might be expected. Therefore, the relationship between  $\delta^{18}\text{O}$  and  $\text{A}^{14}\text{C}$  values (Fig. 29) suggests that locally derived groundwater with high  $^{14}\text{C}$  content mixes continually along flow paths with lower  $^{14}\text{C}$  ambient groundwater.



**Fig. 29** Cross plot of  $\delta^{18}\text{O}$  and  $\text{A}^{14}\text{C}$  data in groundwater in Aquifers A2 (filled circles) and A3 (empty circles)



**Fig. 30** Schematic cross section of groundwater flow in Southern Baldwin County for the year of 2008. Wells located along the North-West and North-East flow paths are not included in the cross section. All wells in the southern part of the study area (Gulf Shores and Orange Beach) are projected on the North-South (A-A') cross section in Fig. 21

Overall, the radiocarbon data indicate that waters in deeper Aquifers A2 and A3 have been recharged beginning in the early Holocene. However, middle and late Holocene recharge waters are pervasive in the aquifer system of Southern Baldwin County. This suggests that water is dynamic in these aquifers and that it is either discharging into the Gulf of Mexico or is being pumped for irrigation and domestic uses.

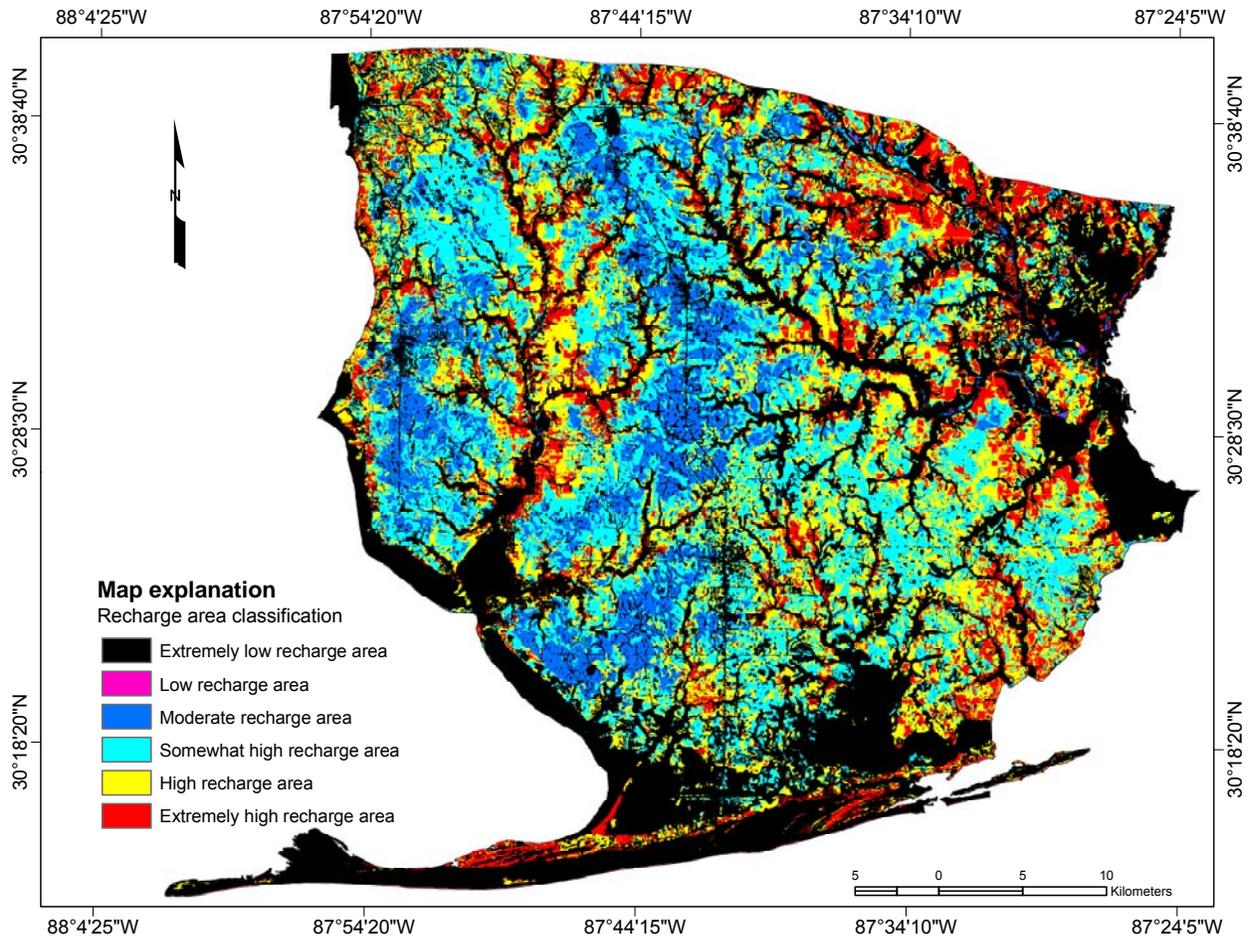
#### Residence Times and Recharge Rates

Groundwater residence times in Aquifer A2 varied up to 3,030 radiocarbon years, while those in Aquifer A3 varied between 305 to 7,600 radiocarbon years. Increasing  $A^{14}C$  values in groundwater were observed down-gradient and with depth, indicating the presence of downward leakage from the upper Aquifer A2 to the lower Aquifer A2 and deeper to Aquifer A3. Based on this information and the spatial location of the dated groundwater samples, replenishment rates are estimated to vary between 0.04 to 0.37 m/yr locally. The highest recharge rates are estimated for the lower Aquifer A2 and upper part of Aquifer A3. Measured groundwater ages for the upper Aquifer A2 range from less than 50 years (i.e. modern waters) to 100 years. Most of the groundwater samples collected from this part of Aquifer A2 exhibit modern ages. It is important to note that residence-time estimations cannot be determined based solely on radiocarbon data. However, recharge rates can be determined using the estimated recharge percentage of total precipitation. Generally, in aquifer systems precipitation is distributed between evapotranspiration to the atmosphere, runoff to surface waters, and recharge to the underlying aquifers. Riccio et al. (1973) estimated that in Baldwin County, 24% of the precipitation is recharged to the aquifer system, 60% goes back to the atmosphere through evapotranspiration, and 16% is runoff to surface water. Therefore, using an average annual precipitation rate of 163 cm/yr for Southern Baldwin County, the recharge rate can be estimated as approximately 0.40

m/yr. Replenishment rates calculated using the radiocarbon data for the lower Aquifer A2 can be approximated as about 0.8 m/yr. Moreover, in Southern Baldwin County, rivers are shallow (<5 m) (Riccio et al. 1973) and generally receive recharge locally. Thus, when estimating recharge rates to the aquifers, this surface component can be neglected. While there is considerable uncertainty associated with these estimates, this translates to an annual average recharge rate of approximately of 0.16 m/yr for Aquifers A2 and A3.

#### Potential Recharge Areas Classification

The recharge area classification was conducted based on several factors that can influence the infiltration of meteoric water to the water table and further to the deeper confined or unconfined aquifers. The most influencing factors are runoff, soil conductivity, soil drainage, and land use land cover hydrological classification. Each one of these factors can impede or facilitate the transport of modern waters to the aquifer system. The recharge area classification indicates that most of Southern Baldwin County area is open to recharge from precipitation with the highest infiltration rates in close proximity to stream and river valleys, forested areas, and around Wolf Bay (Fig. 31).



**Fig. 31** Potential recharge areas classification

### Discussion

The results of this multi-isotopic and geochemical regional study of groundwater evolution and flow dynamics provided an enhanced understanding into the dominant processes controlling the groundwater composition (e.g., isotopic signatures, geochemistry, ages, etc.) and flow regime (e.g., mixing, recharge, discharge, residence times, etc.) for the aquifer system underlying Southern Baldwin County. Estimating radiocarbon ages of groundwater employed the use of naturally occurring stable isotope of carbon in order to identify the source of dissolved inorganic carbon (DIC) in groundwater (e.g., dilution of  $^{14}\text{C}$  concentrations due to limestone

dissolution vs. atmospheric input). Furthermore, a closer evaluation of the  $\delta^{13}\text{C}$  variation offers information on the origin and evolution of groundwater. For Southern Baldwin County, the groundwater  $\delta^{13}\text{C}$  data ranges between -13.5 and -19.2 ‰ indicative of a plant material signature (e.g., Hatch-Slack cycle). This range of values confirms that the groundwater in this area originates from locally infiltrated precipitation through soils extensively cultivated with plants such as corn, grass, and millet, which are widespread in temperate zones (Tamers 1975).

Precipitation provides the primary input to the recharged groundwater. The isotopic composition of groundwaters that are recharged by direct infiltration in temperate zones, are very similar to the mean isotopic composition of the incident precipitation. Good indicators of this similarity are the oxygen-18 ( $^{18}\text{O}$ ) and hydrogen-2 data (D). Based on IAEA WMP monitoring data, the mean  $\delta^{18}\text{O}$  value of precipitation in Southern Baldwin County is approximately -4‰ (VSMOW). The  $\delta^{18}\text{O}$  data for the analyzed groundwater samples ranges between -4.4 and -3.5‰ (VSMOW). This narrow range of values reflects the local meteoric origin of groundwater. Furthermore, this suggests that precipitation infiltrates rapidly to depth and does not undergo significant evaporation at the ground surface. Any evaporation that may take place likely occurs before the precipitation water reaches the land. Generally surface water in temperate zones experiences high rates of evaporation. Therefore, the hydrogen and oxygen signatures are more negative compared to waters infiltrating into the ground without experiencing evaporation. Moreover, because recharge occurs in the absence of evaporation in this area, it can be implied that surface water has negligible contribution to groundwater replenishment. This would also indicate a higher potential for contaminant input to occur from groundwater to surface water bodies such as discharge zones along the coastal margin including estuaries, wetlands, and the Gulf of Mexico in Southern Baldwin County.

Given the regional distribution of the  $\delta^{14}\text{C}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data the results of this study suggest the presence of multiple recharge areas within of Southern Baldwin County considerable groundwater mixing along the flow paths. These processes may explain the presence of unexpected young groundwaters at greater depths along flow paths. Furthermore, the range of the tracer isotope ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) values is an indication of the increased vulnerability to contamination of these highly developed aquifers.

The radiocarbon results from this study revealed groundwaters of modern to paleo-groundwater ages. Modern waters entered the subsurface starting from a few years to several decades before present and are present up to a depth of approximately 70 meters (Figs. 28, 30). Waters with high  $^{14}\text{C}$  activities (modern ages) are confined within Aquifer Zone A2, and for the most part, where the aquifer is under unconfined conditions. The oldest radiocarbon groundwater age was identified on the southernmost well, at Gulf State Park (Table 4; Figs. 28, 30). This well is tapped in Aquifer A3 at a depth of approximately 152 m. This can be explained by the fact that in this area the deep, confined Aquifer A3 is presumably not readily available to recharge from surface or from the shallower Aquifers A1 and A2 and therefore groundwater experiences longer residence times from more distal sources of recharge. However, given the fact that  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the southernmost and deepest samples may indicate influx of seawater from the Gulf of Mexico, some of the residence times may be overestimated. The age distribution demonstrates that waters recharged after 1953 (post-bomb pulse waters) have recharged to approximately 70 meters below land surface. Based on this distribution, we estimate an average vertical velocity of about 0.8 m/yr corresponding to an average groundwater recharge rate of 0.4 m/yr.

Recharge is a fundamental component of groundwater systems and can significantly affect the groundwater flow dynamics and residence times occurring through aquifers. Isotopic

and geochemical analyses of groundwater have been used in order to provide a hydrologic assessment of the flow system in Southern Baldwin County. For example, isotope data allow the classification of groundwater into younger than 50 years, older than 50 years, and mixed waters. Recharge rates calculated using the radiocarbon data are relatively high but are consistent with the highly permeable aquifer material, relatively depleted concentrations of oxygen-18 and hydrogen-2 data (Fig. 23), and with the high occurrence of local recharge areas (Fig. 31). These results are also in agreement with the lack of an observed trend between carbon-13 data and aquifer depth. Recharge rate is estimated by measuring the time it takes water to travel to a certain depth within the aquifer. Due to the highly permeable nature of these aquifers, water from precipitation is expected to be highly influenced by vertical gradients and migration. Hence, rather than recharging water traveling along shallow flow paths within the upper portions of the aquifer (along the topography) to the Gulf of Mexico, water flow regimes can quickly descend as deep as 70 meters below land surface and travel along extended flow paths. Therefore, the vertical hydraulic gradients are likely to be higher in the upper Aquifer A2 than the horizontal gradients. Under this regime recharge water will initially travel vertically into the lower Aquifer A2 and Aquifer A3, and then travel southward, discharging to the Gulf of Mexico. Based on the distribution of the radiocarbon concentrations and estimated velocities, it is most likely that freshwater discharge into the Gulf of Mexico is from Aquifer A3. In a previous study, Robinson et al. (1996a) point out the high transmissivity of the aquifers underlying Baldwin County and consider that these coarse siliciclastic unconsolidated sediments are responsible for transmitting water to a depth very fast and are part of the end-members which are contributing waters to the Gulf of Mexico (i.e. submarine discharge).

## Conclusions

Isotope measurements complement geochemical and hydrogeologic observations by providing identification of source waters and recharge rates. However, when applying these methods to regional and complex flow systems, data interpretation becomes very difficult. This is in part due to the presence of multiple recharge areas that contribute water to the groundwater flow. In addition, groundwater development is another factor that complicates data interpretation. In the groundwater flow system of Southern Baldwin County, age determination is further complicated by mixing of different end-member waters. The hydrogeology of the investigated area also complicates age and source determination because it appears that locally confining layers allow migration of groundwater between shallower and deeper aquifers. In some cases, unconfined aquifers may become locally confined due to the presence of small and intermittent underlying clay layers. Therefore, data interpretation must consider the degree to which mixing occurs and must be consistent with the hydrogeologic data. The results of this study suggest that the narrow variation of the carbon, oxygen, and hydrogen isotopic data can be explained by modern environmental conditions and mixing processes. This is further supported by the occurrence of unexpected older groundwaters in the upper Aquifer A2, and younger (less than 1000 years) groundwaters in the deeper parts of Aquifer A2 and Aquifer A3. The groundwater analyses of this study indicate that the aquifer system in Southern Baldwin County is a highly dynamic system experiencing mixing of recent recharged waters with older, ambient groundwaters. These processes and the evolution of water in this system is supported by previous groundwater studies of the region. It is well documented that Baldwin County experienced intense dry conditions over the last few years. Based on the precipitation data from the National Climatic Data Center (NCDC 2008), Baldwin County experienced increasing drought conditions from 1999. As a result of this decreased source of recharge and reported increases in pumping

from irrigation and public supply wells significant cones of depression have resulted. Under these conditions rain water can recharge rapidly to the depth due to the increased gradients from greater pumping in the region. Accordingly, high  $A^{14}C$  waters were induced downward through the aquifer and mixed with lower  $^{14}C$  waters at the well. Even if pumping at the wells was stopped until the static water level was attained, the probability of sampling ambient groundwater during periods of drought is considerably low. The ease to which groundwater is drawn downward from the upper parts of the aquifer system to the lower aquifer system (i.e. Aquifers A2 and A3) can be explained by the highly conductive sediments that compose the aquifer matrix. Moreover, these observations and isotopic data explain the presence of high vertical gradients in the aquifer system of Baldwin County.

The lack of variation of  $\delta^{18}O$  values and the similarity to the regional precipitation  $\delta^{18}O$  data reflects primary mixing of different end-member waters, and the input of local recharge waters to greater depths. Moreover, given the regional patterns of oxygen-18, hydrogen-2, carbon-13, and carbon-14 isotope results suggest that multiple recharge areas within this geographic area exist and are controlled by mixing during transport (due to naturally occurring and induced gradients). The analyses indicate that  $^{14}C$  concentrations are influenced by mixing processes that occur in a regional and highly developed groundwater system such as that of Southern Baldwin County. Additionally, the mixing theory is validated by previous nitrogen and oxygen isotope studies in region. This study demonstrates that groundwater dating and stable isotope analyses are useful tools for evaluating the vulnerability of aquifers to sources of anthropogenic contamination. As part of this study, this type of data was used to determine the direction and velocity of ground-water flow, and calculate recharge rates for the aquifers underlying Southern Baldwin County. However, it should be noted that groundwater ages,

residence times, and recharge rates estimated for this study are relative and can exhibit variation as they are determined from aquifers under high stress conditions as a result of drought and correspondingly high pumping rates.

This groundwater study improved the understanding of the regional and local groundwater dynamics (i.e. flow paths, residence times, and recharge effects) in the aquifer system beneath Southern Baldwin County. The isotopic survey was vital for the development of a more accurate conceptual model and to enhance the understanding of this dynamic groundwater system and others similar to it.

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## NITRATE DISCHARGE TO COASTAL WATERS IN RESPONSE TO VARIABLE-DENSITY GROUNDWATER FLOW

### **Abstract**

Many coastal aquifers worldwide are being severely stressed as a result of overpumping and related increases in aquifer vulnerability to contamination. The velocity field in coastal aquifers appears to be complicated by the influence of the saltwater wedge. This study aims to evaluate the groundwater flow and nutrient fluxes from the aquifer system of Southern Baldwin County to the Gulf of Mexico in response to variable density flow caused by the presence of seawater at the coast. A regional scale coupled variable-density groundwater flow and transport model was developed to characterize and enhance the understanding of complex groundwater flow dynamics, contaminant transport processes, and contaminant flux to coastal surface waters in these aquifers. As a proxy for a number of contaminant types, the variable-density SEAWAT code was used to simulate hydrologic processes influencing groundwater flow and contaminant transport to the Gulf of Mexico and coastal surface waters. Model input parameters were acquired from published experimental measurements and theoretical data. Constant concentrations of the residual nitrate were uniformly distributed at the surface based on published contamination source areas. Using the calibrated flow model, several scenarios were conducted in order to match as closely as possible simulated contaminant transport trends and concentrations with the observed ones. The simulation results indicate that in the investigated aquifer system complexities arise because groundwater flow dynamics and contaminant transport are additionally influenced by density variations that can occur from the incursion of saltwater.

Residual nitrate concentrations in the saturated zone were estimated to range between 30 to 160 mg/L for the contamination source zones. Simulation results indicate that nitrate concentrations as high as 5 mg/L extend to the deeper Gulf Shore Aquifer (Aquifer A2). Furthermore, the nitrate sources at this depth were released approximately 100 years ago. Vertical and horizontal nitrate transport is attenuated as a result of dilution by dispersion. Simulated nitrate transport trends and concentrations are very similar to field observations. Vertical gradients and mixing appear to be significant in this system. The SEAWAT model results reveal the importance of the Intracoastal Waterway in acting as a groundwater and contaminant sink for the Beach Sand and Gulf Shores Aquifers. The model predicts that the Beach Sand and Gulf Shores Aquifers will be impacted by severe saltwater intrusion, whereas the deeper 350 and 500-foot Aquifers will experience no saltwater intrusion for the entire 1,000 year simulation period. Consequently, nitrate discharge to the Gulf of Mexico originates from the lower part of the aquifer system through submarine groundwater discharge.

### **Introduction**

Discharge of groundwater to coastal water bodies is widespread and occurs as seepage anywhere that an aquifer is hydraulically connected with the sea through permeable sediments and rocks. This process only occurs under the condition of higher-than-sea-level pressure head of the coastal aquifer (Emery and Foster 1948; Manheim 1967). Groundwater discharges to the sea through a freshwater/seawater mixing or transition zone. A literature review of nutrient/nitrate contamination of groundwater and surface waters in coastal areas revealed submarine groundwater discharge as an important source of nutrients and other dissolved chemicals to these systems in general (e.g., Valiela et al. 1990a; Umezawa et al. 2002; Paytan et al. 2006).

However, the magnitude at which these contaminants are delivered to coastal waters through the groundwater discharge remains uncertain.

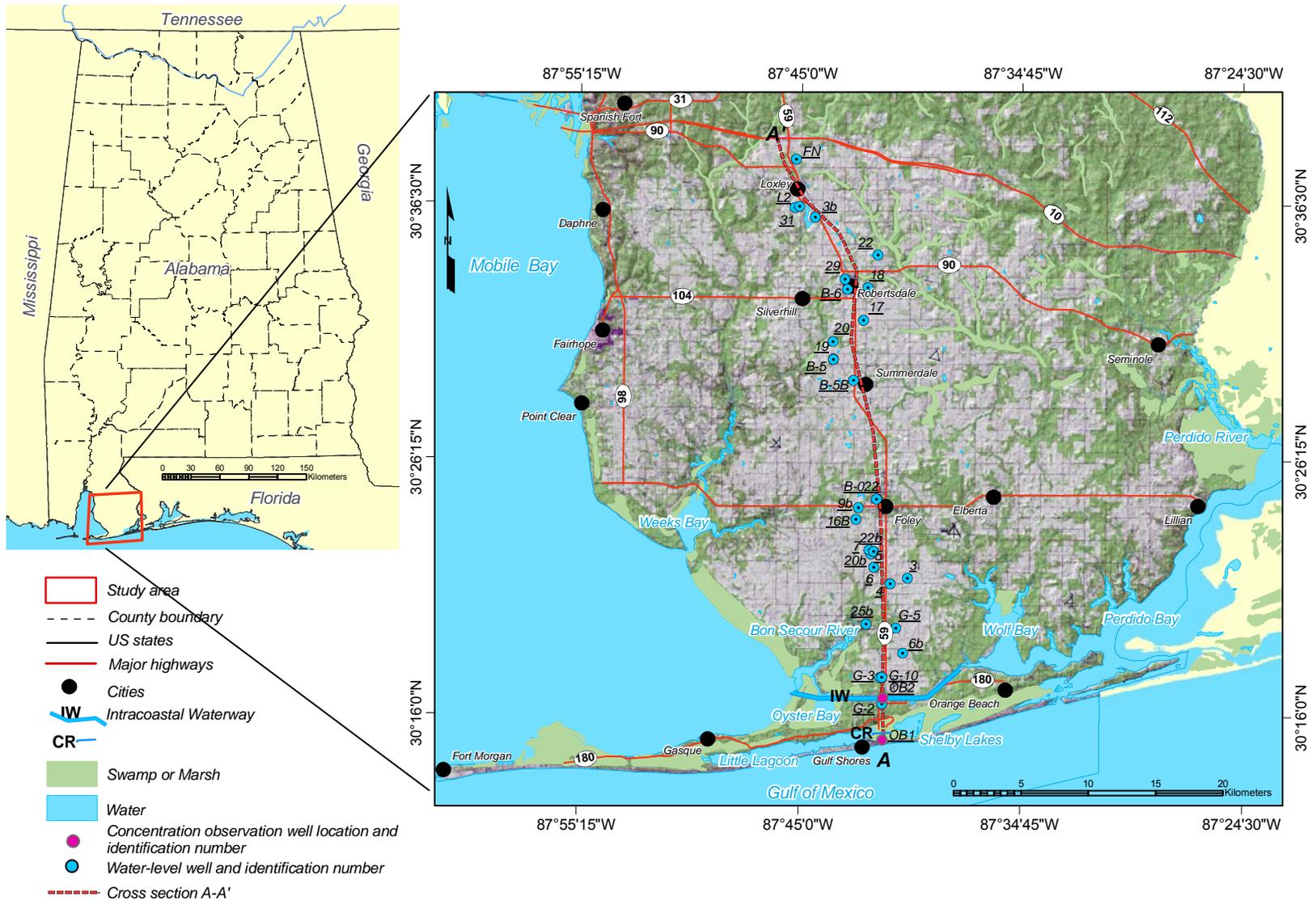
The development of groundwater aquifers in Southern Baldwin County, as sources of freshwater for industry, agriculture, recreation, and as water supplies, poses a potential saltwater intrusion problem of the principal aquifers. Unsustainable groundwater extraction or aquifer overdevelopment throughout coastal Alabama during periods of drought and decreased recharge and for seawater spray during storms may lead to the incursion of salt water into freshwater aquifer zones, shifting the natural freshwater/salt water interface further inland (Murgulet and Tick 2007). This can compromise groundwater quality due to elevated levels of salinity, rendering the water supply unsuitable for various purposes such as drinking water. In addition, the quality and quantity of water discharging to coastal waters may be impacted due to changes in hydrologic conditions caused by fluid density differences and other reactions that occur between aquifer solids and the saline water. Nutrient fluxes from groundwater to the ocean are dependent on the subsurface transport behavior (e.g., removal by denitrification or conservative contaminant behavior) and groundwater velocity near the shoreline. In the study area, nitrate does not undergo denitrification, and therefore behaves as a conservative contaminant (Murgulet and Tick 2009a). A previous study indicated that nitrate is present in very low concentrations or absent in the coastal area of Alabama (Murgulet and Tick 2008), which may be caused by the presence of seawater at the coastline and the Intracoastal Waterway that impacts nitrate transport rates to the Gulf of Mexico and coastal surface waters. As a result, it is important to account for variable-density groundwater flow when quantifying the groundwater and groundwater nutrient flux to the coast.

Various studies such as Marsh (1977), Capone and Bautista (1985), McLachlan and Illenberger (1986), and Simmons (1992), among others, documented the importance of nutrient fluxes from coastal aquifers to the marine environment. Glover (1959) suggested that fresh groundwater flows out to the sea through a narrow seepage facet with a width believed to be nearly proportional to the volume of freshwater flow. The discharged groundwater is brackish toward the seaward edge of the aquifer because of entrainment of salt water from the diffusion zone (Cooper 1959). An underlying saltwater wedge typically intrudes beneath the freshwater aquifer along marine coastlines. This wedge impedes the downward mixing of lighter groundwater and thus magnifies the tendency for groundwater from unconfined aquifers to discharge close to the shore.

The velocity field in coastal aquifers appears to be complicated by the influence of the saltwater wedge (Uchiyama et al. 2000). Previous studies have not taken into account the spatially variable flow field when simulating nitrate flux to the coastal waters. This study aims to evaluate the groundwater flow and nitrate transport in the aquifer system of Southern Baldwin County and to the Gulf of Mexico in response to variable density flow caused by the presence of seawater at the coast. To aid in accomplishing the objectives of this study, a two-dimensional variable-density groundwater flow model was developed using the SEAWAT code (Guo and Langevin 2002).

### **Site Description**

The Southern Baldwin County study area (1,626 square kilometers) is located in the Coastal Plain of South Alabama, South of Interstate 10 (Fig. 32). The area is bounded by the Gulf of Mexico on the South and by Mobile Bay, Perdido Bay, and the Perdido River on the West, Southeast and East, respectively (Fig. 32).



**Fig. 32** Cross section location and selected wells used for model calibration in the Southern Baldwin County area

The coastal regions of Baldwin County are characterized by a robust economy and increasing rate of development. The major land-use/land-cover (LULC) classes in this area are water, developed, barren, natural forested upland, natural shrubland, natural/semi-natural vegetation, planted/ cultivated, and wetland (Homer and others, 2004). Most of the area is dominated by cultivated crops (e.g., agriculture) and deciduous forest (Homer and others 2004).

The physical features of Southern Baldwin County are representative of a typical coastal environment. The primary physiographic units representing Southern Baldwin County include the Coastal Lowlands or “Pine Meadows” unit, and the Southern Pine Hills unit (Fenneman 1983). Soils in this area are mostly sandy with high permeabilities (soil vertical conductivities are as high as 8 meters per day (m/d)). Therefore, precipitation infiltrates relatively fast, resulting in the absence of flowing streams. Water from precipitation percolates to the water table, becoming part of the aquifer system, flowing toward discharge areas, where it intercepts the land surface, in a river/channel, lake, bay, or Intracoastal Waterway.

### Stratigraphy

The stratigraphy of Southern Baldwin County, as well as that of coastal and offshore Alabama, consists of relatively thick Jurassic to Holocene sediments (Chandler et al. 1985). At relatively shallow depths, interbedded sands, silts, gravels and clays comprise the middle Miocene to Holocene sedimentary rocks which host the freshwater aquifer zones of the Baldwin County area. The thickness of these sediments regionally decreases towards the Gulf of Mexico. The sediments are part of three widely recognized geologic units defined by Reed (1971) as: 1) the Miocene Series undifferentiated; 2) the Citronelle Formation; and 3) alluvium, low terrace, and coastal deposits. These three stratigraphic units crop out along different areas within the study area. The lower part of the middle and upper Miocene sediments in Southern Baldwin

County consist largely of clay (the Pensacola Clay) that crops out throughout Mobile, Baldwin, and Washington Counties in Alabama (Walter and Kidd 1979). The overlying middle and upper Miocene coarse siliciclastics consist of interbedded sands and gravels, with sporadic clay lenses (Walter and Kidd 1979). These sediments have a thickness ranging between 3 and 33 meters, are of marine and estuarine origin, and crop out in the northeastern part of the study area.

Interfingering of the lower Pensacola Clay with the upper undifferentiated sediments has been documented by Walter and Kidd (1979) to occur in southernmost Baldwin County. Overlying the Miocene Series undifferentiated are the fluvial sands and clays of the Pliocene-Pleistocene Citronelle Formation. This section consists of nonfossiliferous-clastic sediments and was described by Reed (1971) as “reddish brown gravelly sand”. The alluvial, low terrace and coastal deposits comprise a complex of beach, lagoonal, estuarine, dune, and deltaic sediments that were transported and deposited along lowland areas during the late Pleistocene to Holocene (Walter and Kidd 1979).

## Hydrogeology

Aquifer characteristics, such as transmissivity and hydraulic conductivity, vary spatially throughout the study area as a result of variations in past depositional settings. The groundwater flow direction is primarily towards areas of active discharge such as wells and large bodies of water like the Gulf of Mexico, Bon Secour River and Bon Secour Bay, Weeks Bay, and Oyster Bay. Hence, the general direction of regional groundwater flow is South, South-Southeast and South-Southwest, depending on the regional discharge zones. The hydrologic system of Southern Baldwin County is a result of interactions between geological and physical environments and water. The aquifer system beneath Southern Baldwin County was divided originally by Walter and Kidd (1979) into four aquifer units which are, in decreasing order: the Beach Sand Aquifer,

the Gulf Shores Aquifer, the 350-Foot Aquifer, and the 500-Foot Aquifer. Later these units were grouped into three distinct units at the most southern portion of the study area, based on their stratigraphic association: Aquifer Zone A1 which corresponds to the Beach Sand Aquifer, Aquifer Zone A2 including the Gulf Shores Aquifer and Aquifer Zone A3 which includes the 350- and 500-Foot Aquifers (Chandler et al. 1985) (Fig.33). For the purpose of this study, a combination of the later classification (Fig. 33) of Chandler et al. (1985) with the more detailed hydrologic classification of Walter and Kidd (1979) is employed. Although each aquifer is distinctive, based on hydrologic features, their exact delineation is challenging, as these aquifers respond to long-term hydraulic stresses as a single unit. However, the deeper 500-Foot Aquifer, corresponding to the lower Aquifer A3, has the least hydraulic connection with the upper aquifers.

#### *Beach Sand Aquifer (Aquifer Zone A1)*

The upper unit, known as the Beach Sand Aquifer or Aquifer Zone A1, with a thickness of approximately 15 m is an unconfined aquifer consisting of white fine- to coarse-grained quartzose sands, silt, and locally sandy clay (Chandler et al 1985). Although used mainly for domestic purposes, the Beach Sand Aquifer has a capability of producing more than 100 gallons per minute ( $545 \text{ m}^3/\text{day}$ ) locally. Regionally, Chandler et al. (1985) estimates that this aquifer can yield up to  $1.5 \times 10^5 \text{ m}^3/\text{day}$ , however, only a fraction of that amount can be exploited due to the potential of salt water intrusion.

The Beach Sand Aquifer corresponds to the alluvial, low terrace, and coastal deposits of Pleistocene-Holocene age in lowlands areas (Chandler et al. 1985). This aquifer overlies a continuous, plastic, green-to-gray clay (C1) with an approximate thickness of 6 m. This clay unit serves as a semipermeable hydraulic boundary that separates the Beach Sand Aquifer from the

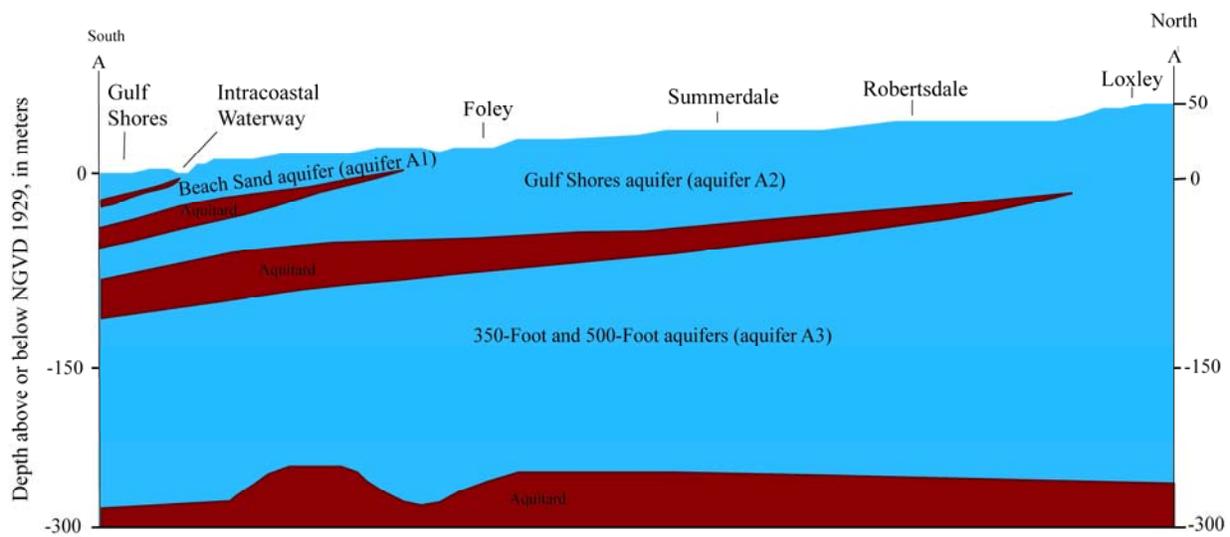
underlying Gulf Shores Aquifer and extends just South of the Intracoastal Waterway (Fig. 33) (Gillette et al. 2000).

This aquifer zone receives recharge from rainfall infiltrating the surface sands, but this fresh water is lost as the result of discharging by downward infiltration to underlying zones and to the Gulf of Mexico. The upper surface of the zone is represented by the water table, which generally conforms to topographic trends, and may fluctuate seasonally as much as one meter. During periods of high precipitation, the depth to water along this zone may be as little as 1.2 meters below the ground surface. Larger water table fluctuations may be observed during periods of minimal precipitation or drought where depth to water may be as much as 5 meters below the ground surface. The Beach Sand Aquifer is subject to impacts from storm events and salt-water spray, particularly in low-lying areas, and is vulnerable to contamination owing to overdevelopment and irrigation practices (Chandler et al. 1985).

#### *Gulf Shores Aquifer (Aquifer Zone A2)*

The middle unit, known as the Gulf Shores Aquifer or Aquifer Zone A2, extends from approximately 20 to 75 meters below ground level (Walter and Kidd 1979). This aquifer varies from confined to semi-confined to unconfined throughout the extent of the study area. The unit consists of three hydrologic units: the upper sand (upper Aquifer A2), the aquitard (C2), and the lower sand (the lower Aquifer A2). The upper sand is generally about 23 m thick and consists of subangular to subrounded, medium- to coarse-grained and moderately-to poorly-sorted quartzitic sand (Walter and Kidd 1979). Within this unit, the local occurrence of clay, sand, and gravel lenses is common. Along Gulf Shores and Orange Beach, the upper and lower sands are separated by a marine clay layer which appears to thicken westward (Chandler et al. 1985) and completely pinches out northward, towards the city of Foley. This aquitard ranges in thickness

from 12 to 27 m and consists of interbedded and interfingered silts, very fine-grained sands, and clays (Walter and Kidd 1979). A 7-day pumping test of the upper sand unit and water levels recorded from both upper and lower sands indicate that the aquitard permeability is one-tenth that of the sands (Walter and Kidd 1979). The lower unit of the Gulf Shores Aquifer, ranging from 15 to 27 m in thickness, is composed of numerous clay and silt lenses. This unit varies both vertically and horizontally from very fine-grained to coarse-grained, subangular to subrounded, poorly sorted and moderately sorted sand (Walter and Kidd 1979).



**Fig. 33** Generalized hydrogeologic cross section of Southern Baldwin County along line A-A' shown in Fig. 32 (modified from Gillett et al. 2000)

Along the southern extent of the study area, the Gulf Shores Aquifer is hydraulically separated from the Beach Sand water-table aquifer on a regional scale (Kidd 1988). However, the marine clay separating the two aquifers pinches out to the North, hydraulically connecting the aquifers into one primary aquifer unit (Fig. 33). The aquifer sediments are part of the Citronelle Formation and the upper Miocene Series undifferentiated geologic units. The aquifer is extensively developed as a source of fresh water for municipal, industrial, private and irrigation wells. Production rates from this unit range from 100 to 1,000 gallons per minute (545

to 5,450 m<sup>3</sup>/day). Recharge to this aquifer zone occurs from rainfall where the unit crops out to the North under unconfined conditions (Chandler et al. 1985) and through downward infiltration from the overlying aquifer units. Clay lenses distributed throughout the Gulf Shores Aquifer can produce semi-confined conditions within the aquifer; however, the aquifer is vulnerable to surface contamination toward the North, as it becomes unconfined.

### *350-Foot and 500-Foot Aquifers (Aquifer Zone A3)*

The lower unit, known as the Deep Miocene Aquifer or Aquifer Zone A3, includes the 350-Foot and 500-Foot Aquifers described by Walter and Kidd (1979). The 350-Foot Aquifer is generally continuous and is encountered at an approximate depth of 107 m (350 feet) in the southern half of the area (Walter and Kidd 1979). This unit is overlain by approximately 30 m of semi-permeable clays and silts (Walter and Kidd 1979). The aquifer varies in thickness from approximately 6 m at the coast to over 30 m around Foley, and becomes wider as the clays pinch out northward (Walter and Kidd 1979). The sands and silts that compose the 350-foot aquifer include interbedded clay lenses of varying extents.

Underlying the 350-Foot Aquifer is a clay layer (C3) about 15 m thick that behaves as an aquiclude and hydrologically or hydraulically separates it from the deeper 500-Foot Aquifer (Walter and Kidd 1979). Permeabilities of the upper part of this aquiclude were recorded to be  $7.9 \times 10^{-8}$  m/s (Walter and Kidd 1979).

The 500-Foot Aquifer contains more uniform and extensive sands, and is encountered at an approximate depth of 152 m. This hydrologic unit, lithologically similar to the Gulf Shores Aquifer, is approximately 15 m thick. However, Chandler et al. (1985) suggests that the hydrologic unit equivalent to Aquifer A3 at the southernmost boundary of the study area extends to approximately 304 meters below ground surface, to the top of the Pensacola Clay. In the

southern part of the study area, within this aquifer, several aquitard layers are interbedded (Walter and Kidd 1979).

The 350-Foot and 500-Foot Aquifers are capable of producing more than 1,500 gallons per minute (8,200 m<sup>3</sup>/day). Groundwater is typically present under confined or artesian conditions in the southern half of the study area. The aquifers receive recharge from infiltrating precipitation where the confining unit is absent and the aquifer unit crops out North of the study area. Additionally, downward infiltration from overlying aquifers may occur as a result of overpumping, or in the absence or discontinuity of the confining layer. A generalized hydrogeological cross section of the study area is depicted in Fig. 33.

#### Water Occurrence and Precipitation

Water enters the aquifer system of the study area predominantly from precipitation through infiltration and a very small amount comes from groundwater inflow (Murgulet and Tick 2009a). Water leaves the aquifer system by flow to surface water, by evapotranspiration, and groundwater outflow. A principal component of the water balance in this area is the groundwater outflow which has been increasing over the last decade or so. As a result of increasing population, tourism and development, groundwater pumping in the region increased from  $2.7 \times 10^7$  L/day to  $1.6 \times 10^8$  L/day between 1966 and 1995 (Reed and McCain 1971; Robinson et al. 1996a). Precipitation is the main source of recharge within the Southern Baldwin County study area. Therefore, recharge is directly influenced by precipitation and infiltration rates.

Precipitation in the southern part of Baldwin County during 2006 averaged approximately 50.8 cm/year (NCDC 2006). Generally, precipitation is distributed between evapotranspiration to the atmosphere, runoff to surface waters, and recharge to the underlying aquifers. Riccio et al. (1973) estimated that in Baldwin County, 24% of the precipitation is recharged to the aquifer

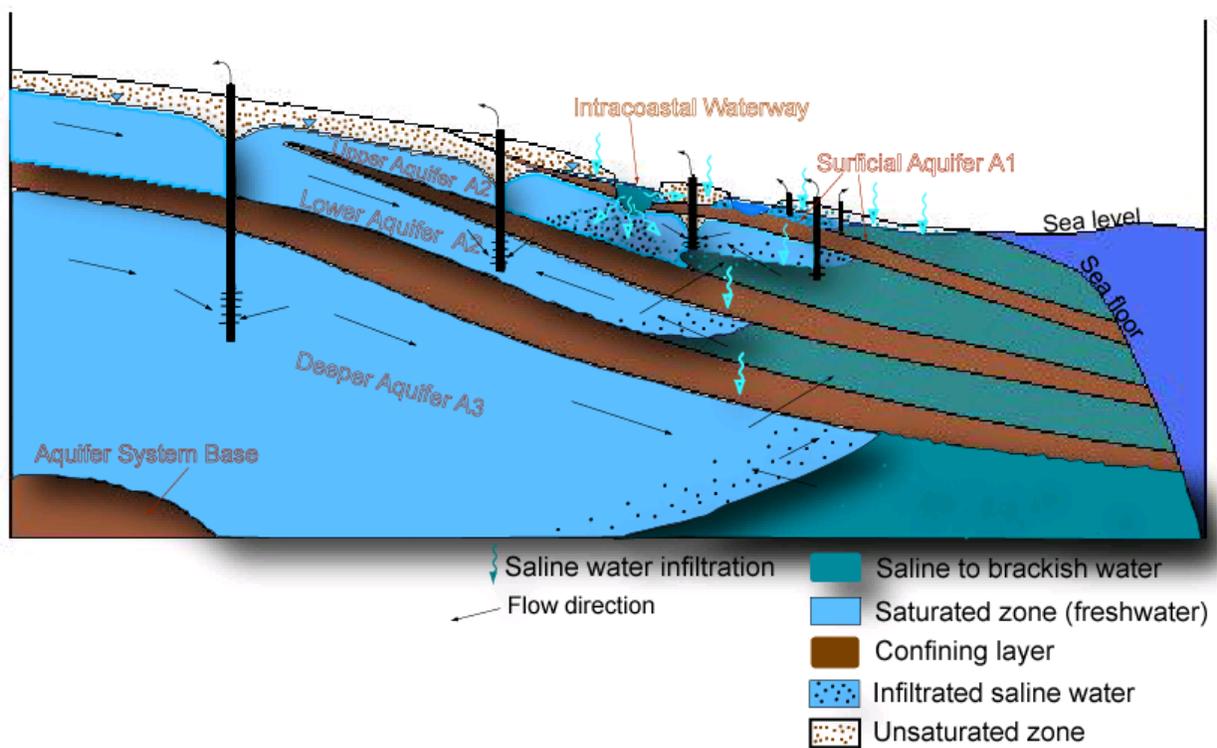
system, 60% goes back to the atmosphere through evapotranspiration, and 16% is runoff to surface water. Within the study area, a relatively minor fraction of the precipitation enters small rivers and streams. The minor rivers within the study region can only accommodate relatively small volumes of water from runoff. In a recent recharge study, Dowling et al. (2004) and Murgulet and Tick (2009a) reported that rain water may infiltrate as much as 40 to 70 meters into the local aquifers. As a result, it was determined that horizontal hydraulic gradients were very low and that the vertical hydraulic gradients were relatively high and mainly downward. The average recharge rates for the region were reported to be  $40 \pm 16$  cm/yr (Dowling et al. 2004; Murgulet and Tick 2009). However, it is important to recognize that recharge and discharge rates are subject to dramatic fluctuation during periods of little to no rainfall. Thus, the static water level data collected for the purposes of this study may not reflect the potentiometric groundwater surface under normal development and precipitation conditions.

#### Saltwater and Nitrate Contamination in Southern Baldwin County

Previous studies in the area conducted by Murgulet and Tick (2007, 2008) indicated the presence of both saltwater and nitrate contamination in the aquifer system underlying the study area. The extent to which the contamination occurred in these aquifers is described in detail in recent studies (e.g., Murgulet and Tick, 2007, 2008).

The saltwater intrusion study indicated that elevated salinity concentrations may have occurred in the Beach Sand Aquifer (Aquifer A1) in regions relatively close to the Gulf of Mexico as the result of a combination of both saltwater intrusion (at the coast) and surface contamination. Saltwater intrusion in the Gulf Shores Aquifer (Aquifer A2) was observed to occur in close proximity to the Gulf of Mexico, East of Gulf Shores (Murgulet and Tick 2007). Their findings were confirmed by field data that exhibited elevated levels of salinity, chloride,

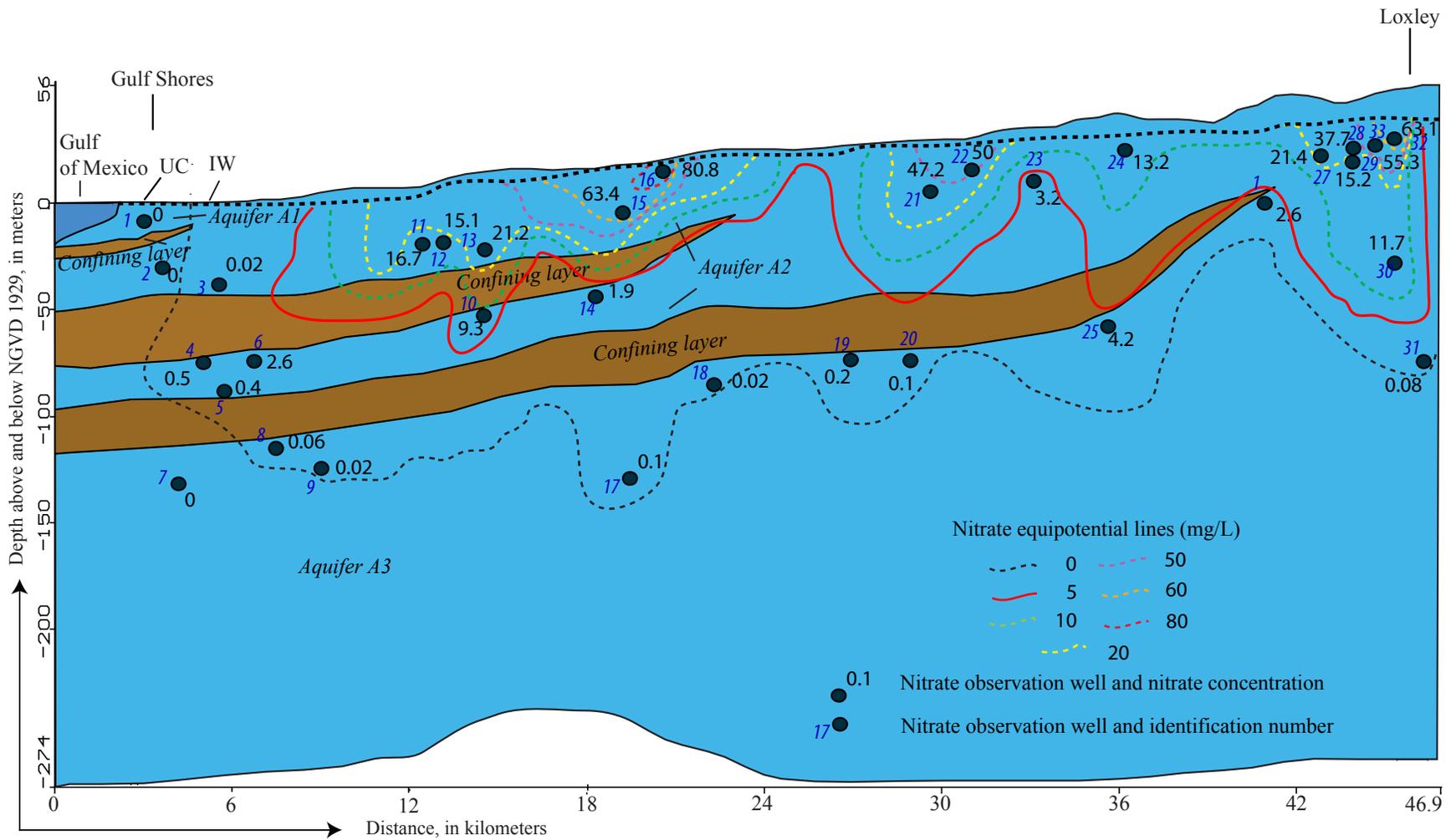
and total dissolved solids for these noted areas. The deeper 350-Foot and 500-Foot Aquifer (Aquifer A3) did not exhibit significant degradation of water quality due to saltwater intrusion. Therefore, the deeper, more confined aquifers seem to be less vulnerable to saltwater intrusion (Murgulet and Tick 2007). However, it should be mentioned that saltwater concentrations in these aquifers may be subject of yearly fluctuations as a result of storm event intensities and variable recharge and discharge rates. In addition, data was limited within the deeper 350-Foot and 500-Foot Aquifer and, as a result, may not fully capture the extent of saltwater intrusion in this region. A generalized representation of the extent of saltwater intrusion/contamination, based on the data collected by Murgulet and Tick (2007), is presented in Fig. 34.



**Fig. 34** Conceptual model of the extent of seawater intrusion/contamination along line A-A' shown in Fig. 32 (modified from Murgulet and Tick 2007)

Nitrate concentrations exceeding regulatory limits (MCL = 45 mg/L as nitrate) were identified within the Gulf Shores Aquifer. Iso-concentration maps for Aquifer A2 reveal three spatially distinct regions impacted by relatively high nitrate concentrations within the study area that may serve as sources of nitrate (Murgulet and Tick 2008). In addition, low to very low nitrate concentrations were observed for the surficial Beach Sand Aquifer and for the deeper 300- and 500-Foot Aquifers. A generalized representation of the extent of nitrate contamination within the investigated aquifer system, based on the data collected by Murgulet and Tick (2008), is presented in Fig. 35.

The cross-sectional model developed for this study intersects two major and two moderately nitrate-impacted areas (Murgulet and Tick 2008) and passes just West of the most extensive seawater contamination/intrusion areas (Murgulet and Tick 2007). In the coastal study area, nitrate is almost absent in all three major aquifers (Murgulet and Tick 2008). Furthermore, nitrate and chlorophyll levels measured for Lake Shelby and Little Lagoon, located South of the Intracoastal Waterway, are extremely low or absent compared to those measured in Weeks Bay and Oyster Bay, located in the northern part of the study area (Murgulet and Tick 2009b).



**Fig. 35** The extent of nitrate contamination along line A-A' shown in Fig. 32 (modified from Murgulet and Tick 2008); the location of nitrate field observation wells is represented in the figure by the black filled circles

### **Numerical simulation of nitrate transport in response to density variable flow**

The nitrate contamination problem in Southern Baldwin County extends over a fairly large area. A three-dimensional approach to this problem would provide information about nitrate transport in all directions towards discharge areas. However, developing a two-dimension cross-sectional model minimizes the simulation time, while offering adequate information about nitrate transport in subsurface to coastal waters in response to variable density flow. In this study the cross-sectional model was developed along a general North-South flow direction, based on the flow gradients identified by Walter and Kidd (1979) and Murgulet and Tick (2007). A numerical model was developed to represent the three major aquifers described in this paper, the Intracoastal Waterway (IW), the unnamed channel connecting Shelby Lakes and Little Lagoon (CR), and the Gulf of Mexico (Fig. 32). The model accounts for processes such as advection and dispersion that may occur within any subsurface system when a contaminant is released under conservative conditions and for the density-difference between freshwater and seawater. Sorption and reaction terms are not included in the simulation, because nitrate behaves conservatively in the absence of denitrification (Murgulet and Tick 2009b).

Although calibrated for flow along cross-section A-A', the outcome of the model is representative for most of the coastal area, given the similarity in hydrologic characteristics. However, different situations may arise as a result of the dissimilar extents of the saltwater intrusion.

The model was calibrated for flow under steady-state conditions using SEAWAT, and then solute transport was simulated under transient conditions. Although no stresses were applied to the system, a transient simulation was necessary in order to account for the density difference between freshwater and seawater with every simulation step. During the transient simulation, the flow field was updated with every time step, based on the change in density. Given the size of

the model and the location of the nitrate sources from the coast, a 1,000 year transient simulation time was necessary in order to allow enough time for the contaminant to reach the coast.

Therefore, using the results from the one year steady-state calibration for flow, the model was simulated under transient conditions for 1,000 years using SEAWAT.

Although the model is not calibrated for nitrate or salinity concentrations, the calibrated flow system used as the initial conditions for the transient model offers a good representation of solute transport under conservative conditions. Moreover, the model reveals seawater movement at the coast under transient conditions, and the resulting groundwater and contaminant transport to the coast in the absence of any hydrological stresses. Developing a groundwater flow model for the area provides the basis for the solute transport model simulating nitrate movement along a flowpaths.

### **Simulation Code**

The last decade has seen the introduction of several density-dependent simulation codes based on the commonly used groundwater model, MODFLOW, developed by the U.S. Geological Survey (McDonald and Harbaugh 1988; Harbaugh et al. 2000). Some of the codes which can be used to simulate seawater intrusion in coastal areas, and groundwater and contaminant transport to coastal waters, are SEAWAT (Guo and Bennett 1998a, b; Guo and Langevin 2002; Langevin et al. 2003), MOCDENS3D (Oude Essink 1998), MODHMS (HydroGeoLogic Inc. 2002), and the SWI Package for MODFLOW (Bakker and Schaars 2003). A summary of these four MODFLOW-based codes was provided by Langevin et al. (2004). Information on various computer codes that have the ability to simulate density-dependent groundwater flow is presented by Sorek and Pinder (1999). The SEAWAT code has proved to be a useful tool for simulating variable-density fluid flow through different and complex scenarios,

including submarine groundwater discharge, brine transport, seawater intrusion in coastal aquifers, and groundwater flow near salt domes. The code has been used to simulate many commonly used benchmark problems (Guo and Langevin 2002; Langevin et al. 2003; Bakker et al. 2004). More applications of the SEAWAT code are described in Bakker et al. (2004), Bakker (2003), Bauer et al. (2006), Dausman and Langevin (2005), Langevin (2003), Langevin et al. (2005), Mao et al. (2006), Schneider and Kruse (2006), and Zimmermann et al. (2006).

To evaluate groundwater and contaminant fluxes in coastal aquifers, the model should account for the density difference between freshwater and seawater (Kohout 1960a). To account for this difference, the code should solve the variable-density groundwater flow and the solute-transport equations (Dausman and Langevin 2005). The SEAWAT code (Guo and Langevin 2002) combines the two commonly used constant-density flow MODFLOW (Harbaugh et al. 2000) and solute transport MT3DMS (Zheng and Wang 1999) codes into a single code that solves the groundwater flow equation for variable density in terms of equivalent freshwater head (Dausman and Langevin 2005). The equation was derived by Guo and Langevin (2002) as follows:

$$\frac{\partial}{\partial x} \left( \rho K_{fx} \frac{\partial h_f}{\partial x} \right) + \frac{\partial}{\partial y} \left( \rho K_{fy} \frac{\partial h_f}{\partial y} \right) + \frac{\partial}{\partial z} \left( \rho K_{fz} \left[ \frac{\partial h_f}{\partial z} + \frac{\rho - \rho_f}{\rho_f} \frac{\partial Z}{\partial z} \right] \right) = p S_f \frac{\partial h_f}{\partial t} + \theta \frac{\partial p}{\partial C} \frac{\partial C}{\partial t} - \rho q_s, \quad (1)$$

Where,  $K_{fx}$ ,  $K_{fy}$ ,  $K_{fz}$ , are equivalent freshwater hydraulic conductivities in the three coordinate directions, respectively [ $LT^{-1}$ ];  $\rho_f$  is the density of freshwater [ $ML^{-3}$ ];  $h_f$  is the equivalent freshwater head [L];  $Z$  is the elevation above datum of the center of a model cell [L];  $S_f$  is the equivalent freshwater specific storage [L-1];  $\theta$  is the effective porosity [dimensionless];  $C$  is the solute concentration [ $ML^{-3}$ ];  $q$  is the density of water entering from a source or leaving through a

sink  $[ML^{-3}]$ ;  $q_s$  is the volumetric flow rate of sources or sinks per unit volume of aquifer  $[T^{-1}]$ ; and  $t$  is time  $[T]$ .

The following solute-transport equation is solved by SEAWAT utilizing MT3DMS routines while allowing for flow updates based on the solute mass:

$$\frac{\partial C}{\partial t} = \nabla * (D * \nabla C) - \nabla * (\bar{v}C) - \frac{q_s}{\theta} C_s, \quad (2)$$

Where,  $D$  is the hydrodynamic dispersion coefficient  $[L^2T^{-1}]$ ;  $\bar{v}$  is the fluid velocity  $[LT^{-1}]$ ;  $C_s$  is the solute concentration of water entering from sources or leaving through sinks  $[ML^{-3}]$ .

The conversion from solute mass to fluid density is obtained using the equation of state developed by Baxter and Wallace (1916):

$$\rho = \rho_f + E * C, \quad (3)$$

where,  $\rho$  is the density of the ambient aquifer water  $[ML^{-3}]$ ;  $E$  is a constant having an approximate value of 0.7143 for salinity concentrations ranging from zero to that of seawater in grams per liter; and  $C$  is the total dissolved solids concentration salinity equivalent  $[ML^{-3}]$ .

### **Spatial Discretization**

The two dimensional finite-difference grid used to represent the model consists of twenty-four layers in order to represent the subsurface hydrogeology of the study area, to allow for a better representation of different lithologies during calibration (e.g., conductivity values), and avoid numerical complications due to variable cell volumes (Fig. 34). All layers vary in thickness to best represent elevations of the specific formations. Layers 1 and 2 correspond to the unconfined Beach Sand Aquifer. Layer 3 is equivalent to the confining unit C1 (Fig. 34). Layers 4 through 6 represent the upper Gulf Shores Aquifer. The confining unit that separates the upper

and lower Gulf Shores Aquifers (C2) is represented in the model by layers 7 through 9. Layers 10 and 11 correspond to the lower Gulf Shores Aquifer. The underlying confining layer (C3) correspond to layers 12 and 13 (C3). The 350 and 500-Foot Aquifers are represented in the model by layers 14 and 15 and 19 through 24, respectively. The aquiclude (C4), separating the aforementioned deeper aquifers, is represented in the model by layers 16 through 18. The deeper 500-Foot Aquifer includes interbedded confining layers at the southern boundary (Walter and Kidd 1979). However, due to limited data, the model does not simulate a continuous confining layer but rather intermittent lower conductivity lenses. The system is considered to be both confined and unconfined. The model grid is 46,850 x 20 meters corresponding to 235 columns and 1 row, respectively. The cell size in the X direction is 199.4 m. The length of the cross section corresponds to the approximate distance between the coastline and a few hundred meters North of Interstate 10 (Fig.32).

### **Boundary Conditions**

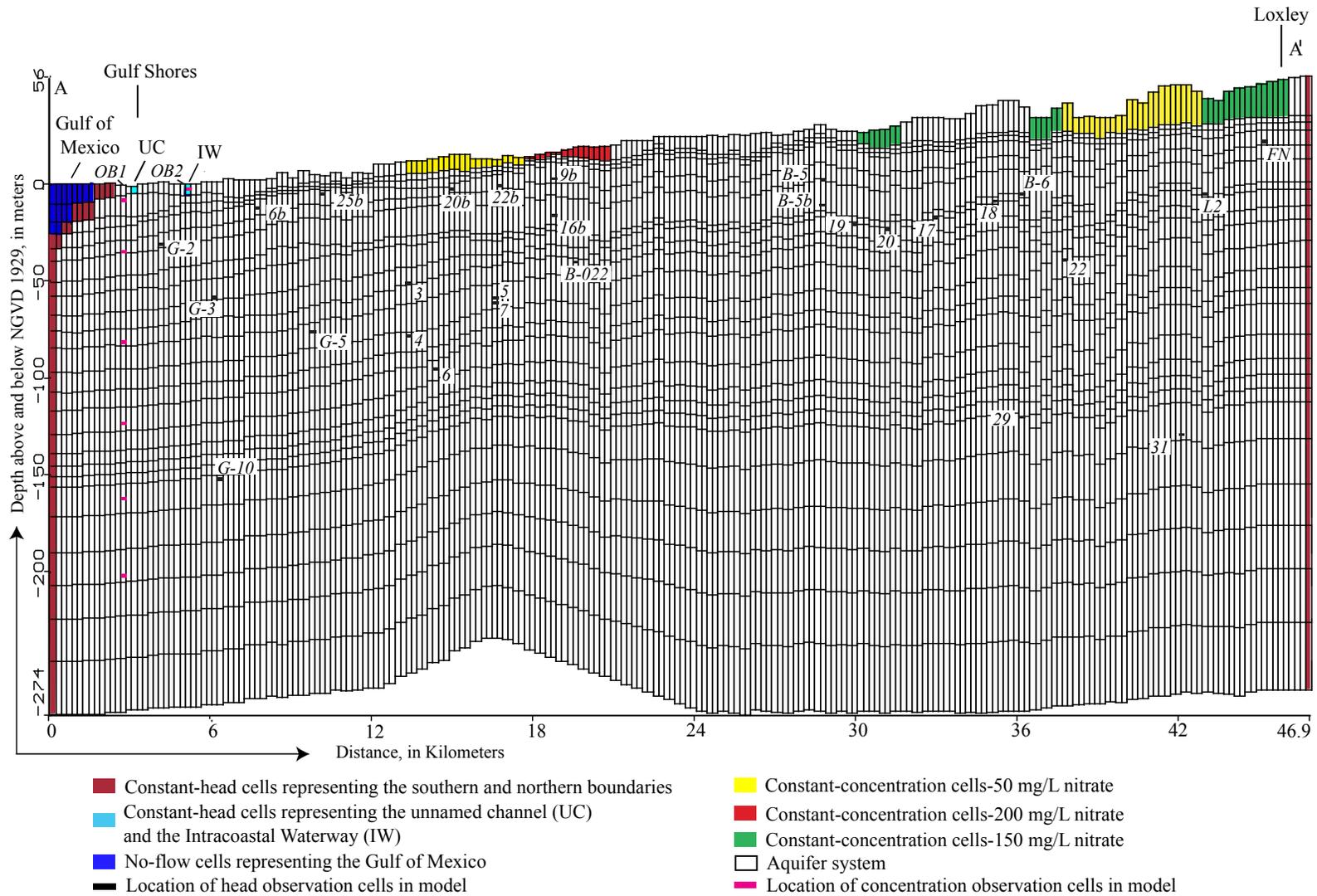
The present model includes boundary conditions such as constant head and constant concentration, no flow, and recharge. Boundary conditions were assumed to be constant for the entire 1,000 years simulation period (Fig. 36).

Constant-head boundaries, for all twenty-four layers, were established along the southern (Gulf of Mexico) and northern boundaries (immediately North of Interstate 10) of the aquifer system in the vertical direction and at the Intracoastal Waterway and the unnamed channel connecting Lake Shelby and Little Lagoon (on layer 1) (Fig. 36). The constant-head boundaries were established to mimic the regional trend of the potentiometric surface and to represent observed water levels for the simulated year conditions. Salinity constant concentrations were assigned at each of the constant head boundaries. Salinity concentrations at the coast vary by

aquifer, based on field observations. Thus, for the Beach Sand and the upper Gulf Shores (upper A2) Aquifers, salinity was set at the concentration of seawater (35,000 mg/L). The salinity concentration for the lower Gulf Shores Aquifer (deeper A2) was set to 10,000 mg/L, and for the 350-Foot (upper A3 Aquifer) and the 500-Foot (deeper Aquifer A3) aquifers salinity concentrations were set at 3,000 and 500 mg/L, respectively. Constant head values assigned at the southern boundary were based on field observations as well. Even though measured salinity concentrations and water levels for the aquifers were not acquired in close proximity to the assigned boundaries, values for these boundaries were based on the observed values at the southernmost observation wells. Moreover, values assigned at the coastal constant head boundaries were set lower than those observed considering that the gradient is towards the coast and therefore the head elevation will decrease. Constant head at the northern boundary of the model was assigned on all active layers and values were set to the average head value observed for each aquifer. Therefore, constant head values for the top 10 and bottom 14 layers were set to 36 and 33.5 m, respectively.

Salinity concentrations assigned at the coastal constant-concentration boundaries were set higher than those observed further inland because it is expected that as approaching the interface, salinity concentrations are increasing. Salinity concentrations were set to 35,000 mg/L in aquifers where the head values are considered close to sea level (represents the Gulf of Mexico waters). Also, a head value equal to the sea level was assigned in aquifers that experienced saltwater contamination further away from the coast (the Beach Sand and the upper Gulf Shores Aquifers). The Beach Sand and upper Gulf Shores Aquifers (layers 1-9) head values and salinity concentrations were set to 0 m and 35,000 mg/L, respectively. Head values and salinity concentrations at the lower Gulf Shores Aquifer (layers 10-13) were set at 1 m and 10,000 mg/L,

respectively. The 350-Foot Aquifer (layers 14-18) constant head and concentration boundaries assigned values were 3 m and 3,000 mg/L, respectively. Observation data for the 500-Foot Aquifer (layers 19-24) were not available and it was assumed, based on published data and the presence of good confining conditions of this aquifer (e.g. low permeability of the overlying confining layer, at the coast), that this aquifer is not impacted by seawater intrusion and that head values will be higher than those of the overlying 350-Foot Aquifer. Consequently, constant head and salinity concentration values were estimated to be 4 m and 500 mg/L, respectively.



**Fig. 36** Model grid and boundary conditions

Constant-head values were set to zero at the Intracoastal Waterway and at the unnamed channel connecting Lake Shelby and Little Lagoon. The input salinity value at the waterway was set to 18,450 mg/L whereas at the unnamed channel was set to 29,750 mg/L. These concentrations were assigned using an average value of two salinity readings from each water body acquired in September 2009. Cells representing the Gulf of Mexico in the Beach Sand Aquifer (Fig. 36) were set as inactive because these cells have no impact on simulation results. All other aquifers are considered to extend for a long distance underneath the Gulf of Mexico (Walter and Kidd 1979). A no-flow boundary was assigned to the bottom of the model because exchange with deeper aquifers is expected to be negligible.

### **Model Calibration**

Most groundwater modeling efforts are deterministic in nature. These models assume that geologic properties are constant throughout a layer of soil or rock formation (Freeze, 1975) and therefore each layer may act as a single homogeneous and isotropic system. This assumption of homogeneity does not accurately reflect nature. In most systems, sediments vary due to the way they are deposited, lithified, and altered by weathering and tectonic processes. These variations and many other factors impede a layer from acting as a uniform system. Hydraulic conductivity, dispersion, and transmissivity can vary significantly over an area and therefore the interpretation of the results is based on assumptions. If not accounted for, these natural variations and resulting heterogeneity of geologic properties will not accurately reflect the behavior of the system being modeled. The model developed for this study, although simplistic in representing hydrogeologic conditions, allows for a large variation of aquifer characteristics.

A one year steady-state SEAWAT simulation was conducted in order to achieve flow calibration and representative aquifer parameters and to provide initial heads and concentrations

for the transient simulation. Constant head and salinity constant concentration boundaries were assigned before the simulation started. Model calibration was achieved through a trial-and-error method, adjusting horizontal and vertical hydraulic conductivity and recharge. Hydraulic head values from twenty-nine observation wells were selected for the calibration (Table 5).

Geographic Information System (GIS) coverage was used to identify well locations and distances from the coastline. The observation wells were located in the model by the distance from the coastline, based on their geographic location. The wells included in the model calibration (e.g., for head observation data and hydraulic properties) are a distance of one kilometer West and East from the cross-sectional line. The wells located outside the cross-section were projected on the line. The location of the observation wells and a summary of the tabulated calibration results with summary statistics are presented in Fig. 37 and Table 5. Consequently, the estimated parameters and the simulation results represent an area of approximately two kilometers centered along cross-section A-A'.

Numerous 1-year simulations were conducted in order to estimate the representative hydraulic conductivity and recharge values and to achieve head calibration. The calibration was conducted until the simulated head values reasonable matched the observed head values (Fig. 37). Successive simulations were carried out with the aim to increase the correlation coefficient, and decrease both the root mean square (RMS) and standard error of the estimate (Fig. 37). The porosity, specific yield, and dispersivity values remained constant during calibration, while the hydraulic conductivity and the recharge values were manipulated. An average porosity of 0.3 was set for the model calibration based on average porosity values for the aquifer system (Walter and Kidd 1979). In the absence of measured specific yield and dispersivity data, average values

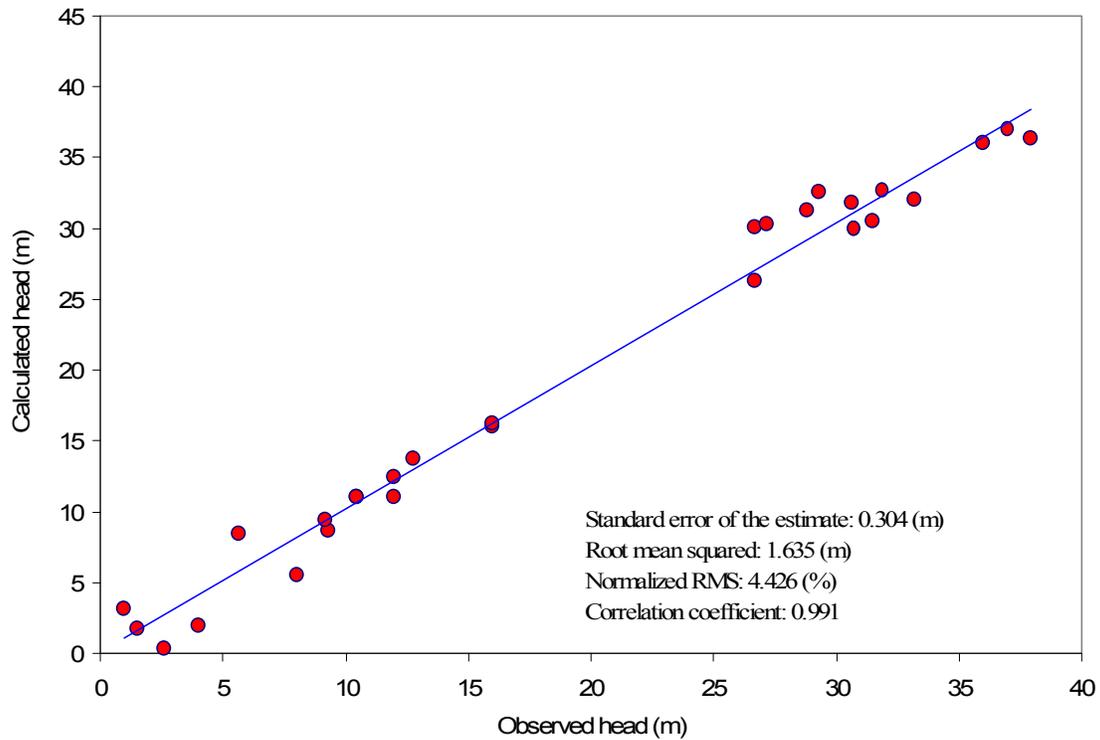
of these parameters found in literature were set to 0.17, and 1 m, respectively for the entire simulation.

Hydraulic conductivity values used for calibration were within the range presented in literature (Walter and Kidd 1979; Chandler et al. 1985; and Gillett et al. 2000) and in available driller's well logs and aquifer descriptions. The average representative longitudinal and vertical conductivity values for the water bearing units ranged from 22.8 to 49.3 m/day and from 1.5 to 5.5 m/day, respectively. However, during the calibration intermittent low conductivity lenses were assigned within the aquifers. In order to reach the best calibration, these aquitard lenses were assigned to either stop water flow further downgradient or to create locally confined conditions.

Recharge, estimated from average precipitation for 2006, was applied at the top of the first layer. Therefore applying the recharge coefficient of 0.24 reported by Riccio et al. (1973) to the 2006 average precipitation rate of 50.8 cm, the recharge rate was set to 12.2 cm/yr. However, during the calibration, recharge rates varied from 0 to 1.50 cm/yr. This may be explained by the absence of pumping in the simulation which represents the main loss of water from the aquifer system. Runoff and evapotranspiration were not simulated in the model because the recharge was calculated by eliminating these two parameters. Hydrogen and oxygen isotope data described by Murgulet and Tick (2009a) indicates that water recharging the aquifers in the study area experience negligible evaporation at the ground surface. An overall correlation coefficient of 0.99 and a root mean square value of 1.635 were obtained for the model as an overall result of the calibration (Fig. 37).

Table 5. Wells used for the calibration in Southern Baldwin County, their distance from the coast and from the model origin, observed and calculated head values, and residual values

Well ID	Model location in the X direction (m)	Distance from the coast (m)	Depth to screen (m)	Measured head (m)	Simulated head (m)	Residual (m)
16b	18,730	17,530	37.22	16.00	16.06	0.06
17	32,921	31,721	52.01	31.48	30.49	-0.99
18	35,047	33,847	50.52	30.70	31.81	1.15
19	29,903	28,703	47.79	26.70	30.12	3.46
20	31,035	29,835	51.90	27.20	30.27	3.09
20b	15,072	13,872	18.28	12.00	11.04	-0.96
22	37,671	36,471	81.42	33.18	32.01	-1.17
22b	16,753	15,553	14.37	12.00	12.43	0.43
25b	10,122	8,922	10.20	1.00	3.15	2.15
29	36,147	34,947	159.63	28.83	31.31	2.48
3	13,443	12,243	63.96	9.30	8.63	-0.67
31	42,046	40,846	180.28	29.30	32.57	3.27
3b	41,233	40,033	56.09	36.00	36.02	0.02
4	13,350	12,150	90.95	5.66	8.41	2.75
5	16,665	15,465	71.67	10.44	11.04	0.60
6	14,280	13,080	108.64	9.17	9.40	0.23
6b	7,762	6,562	15.58	4.00	1.99	-2.01
7	16,665	15,465	74.24	10.44	11.04	0.60
9b	18,844	17,644	17.24	16.00	16.20	0.20
B-022	19,581	18,381	59.62	26.68	26.29	-0.39
B-5	28,718	27,518	28.93	30.80	29.95	-0.82
B-5b	28,737	27,537	41.93	30.80	29.95	-0.82
B-6	36,100	34,900	45.26	31.93	32.70	0.77
FN	45,200	44,000	30.50	37.93	36.35	-1.58
G-10	6,087	4,887	153.40	12.78	13.69	0.91
G-3	6,198	4,998	59.70	1.51	0.32	-2.32
G-5	9848	8,648	81.21	8.03	1.71	0.20
G-2	4,230	3,030	32.89	2.64	5.57	-2.46
L2	42,943	41,743	50.00	37.00	37.00	0.00



**Fig. 37** Scatter diagram showing the goodness of fit between the observed and calculated heads and resulting calibration statistics

The simulated water-level data were compared with the measured water-level data corresponding to the observation wells. There was a remarkably good match between the simulated and observed head-values (Fig. 37), considering that the model does not account for all changes in lithology within the aquifer system or in a confining unit because of the lack of lithologic data for some parts of the area. However, for the central part of the model no water levels were available and therefore the calibration results may not be representative of the steady-state hydrologic conditions.

## Transient Simulation

A 1,000 year simulation was conducted in order to predict nitrate transport to the coast from sources in the simulated area (Figs. 35, 36). The calibrated aquifer parameters and the resulting head-levels were imported as initial conditions for the 1,000 year simulation. The 1,000 year simulation model consists of 60 time steps.

For the 1,000 year simulation, nitrate constant concentrations were assigned at the top of layer 1 (Fig. 36). The location of these cells was chosen based on the nitrate source zones and recharge zones previously identified by Murgulet and Tick (2008, 2009a, b). Nitrate constant concentrations (e.g. layer 1) were assigned based on the type of nitrate source and published nitrate concentrations below specific nitrate source fields (e.g., crop fields, cattle grazing areas, residential areas, turf fields, etc.). Although nitrate concentrations immediately below cattle grazing areas, sewage breakthrough or fertilizer application fields can be extremely high, concentrations that reach the water table usually are reduced due to denitrification occurring within the soil horizons and due to plant uptake. Field observation data indicate the presence of elevated nitrate concentrations at relatively shallow depth (Murgulet and Tick 2008). Nitrate concentrations as high as 5 mg/L were identified locally in the deeper Aquifer A2. These observations suggest the presence of a constant contamination source at the land surface and the top of the water table aquifer. Therefore, it is assumed that nitrate sources will remain constant along the cross section and that there will be residual nitrate in soils, which will be transported to groundwater. The initial input values for nitrate constant concentrations ranged from 50 to 200 mg/L (Fig. 36). Several scenarios were simulated for the nitrate transport in order to attain the best match between simulated and observed nitrate migration trends and nitrate concentrations. For this purpose nitrate concentrations were adjusted with each scenario until the simulation

results agreed the most with the observed results (Figs. 35, 39). Furthermore, an additional simulation scenario aimed to identify the time it will take nitrate to be flushed out of the system assuming that no stresses such as pumping will occur and that the nitrate source will cease to exist after one year from the beginning of the simulation.

Two observation wells were assigned at the Intracoastal Waterway (OB2) and at the coastline (OB1) in order to estimate seaward nitrate discharge and inland movement of the seawater wedge at these locations. The screened interval in the observation well OB2 is set at 3 m below land surface to get estimates of nitrate discharge from both shallow and deeper aquifers. The second well is located between the unnamed channel and the coastline (Fig. 36). Screened intervals for this well were assigned at each of the described aquifers (Fig. 36).

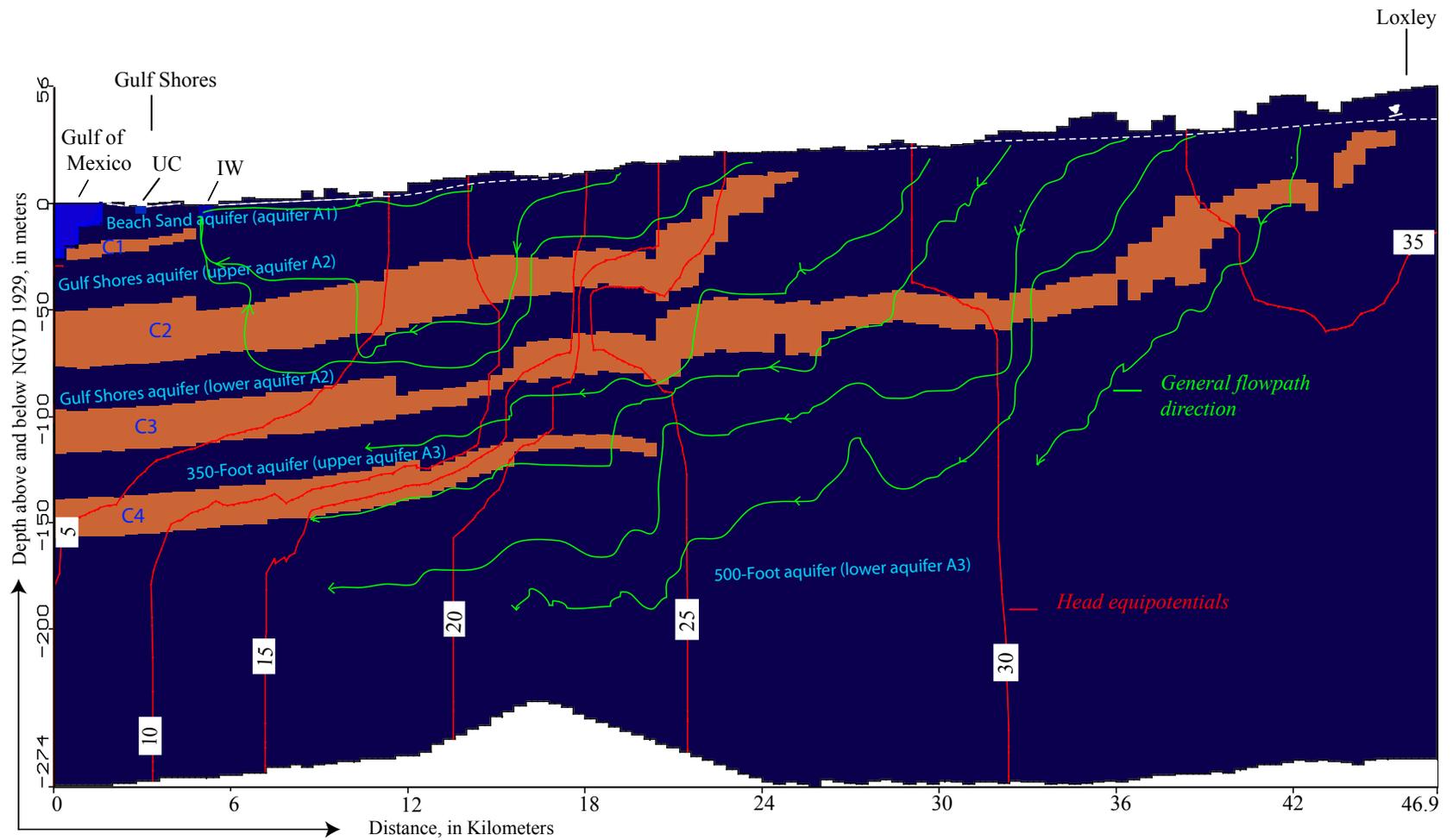
#### Simulated flow and contaminant transport

The simulation results indicate that although the general flow direction is from North to South, an induced inverse gradient exists from South to the Intracoastal Waterway. This is explained by the fact that the water level in the Intracoastal Waterway is equal to sea level, creating a gradient from both North and South directions. Thus, water in the upper and lower Gulf Shores Aquifers flows southward and then upward to the channel (Fig. 38). Particle tracking was used to identify flow patterns (Fig. 38) and travel times. Most of the recharge in the northern part of the study area infiltrates locally and becomes part of the southward flow within the deeper Gulf Shores and the 350-Foot Aquifers. Water from the 350-Foot and 500-Foot Aquifers discharges to the Gulf of Mexico through submarine groundwater discharge (Fig. 38). Groundwater residence times in the shallower parts of the aquifers ranges from less than one hundred to a few hundred years. However the time increases as water flows locally through semiconfining layers or lenses. In the deeper parts of the aquifer system, residence times exceed

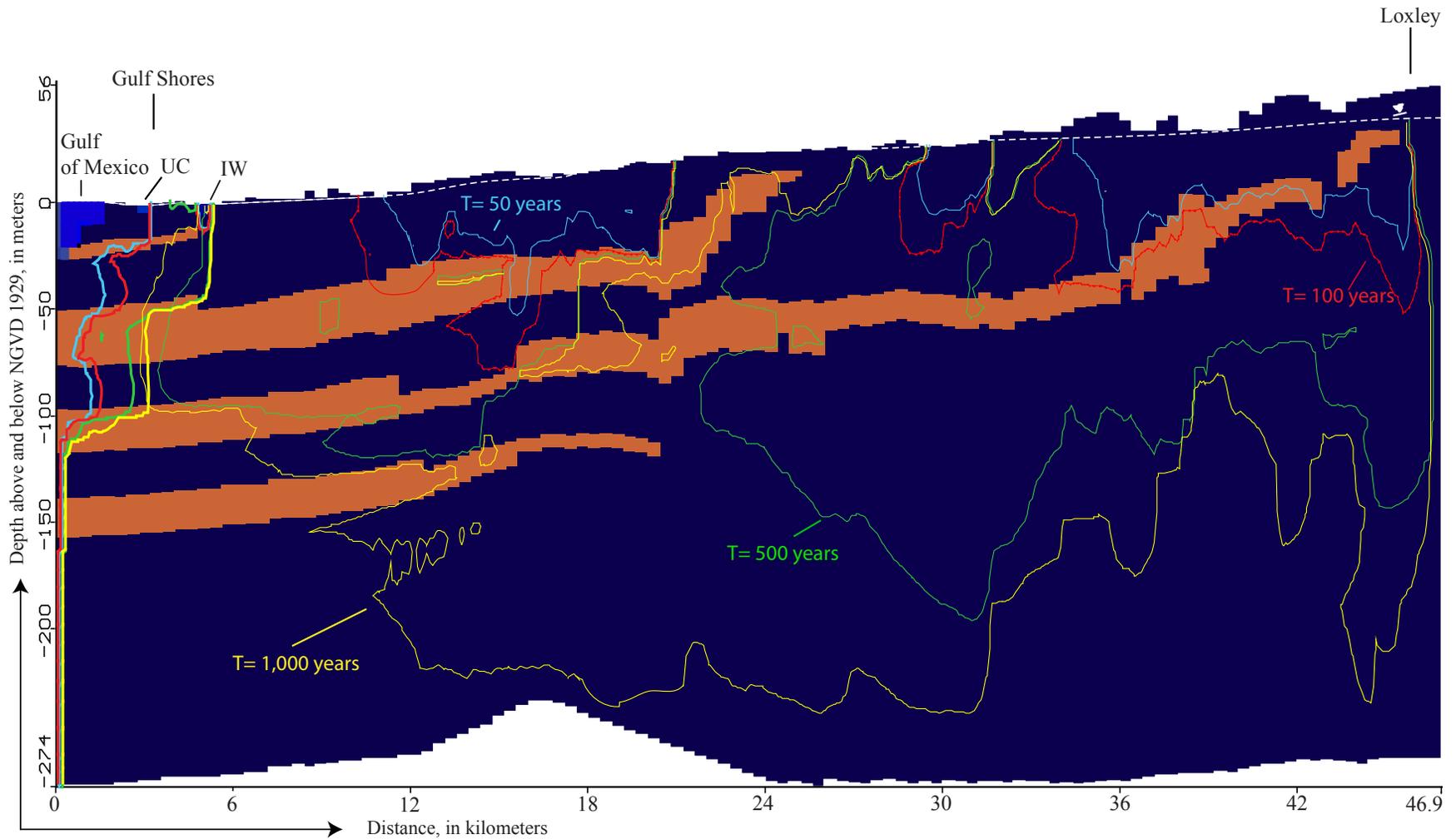
1,000 years. Locally, within the Gulf Shores Aquifer, lower residence times were simulated as a result of high vertical gradients.

The model results reveal the importance of the Intracoastal Waterway in acting as a groundwater sink for the Beach Sand and Gulf Shores Aquifers. The high gradient near the Intracoastal Waterway denote the high impact of this type of water body on groundwater flow towards the gulf and other coastal water bodies (e.g. the unnamed channel).

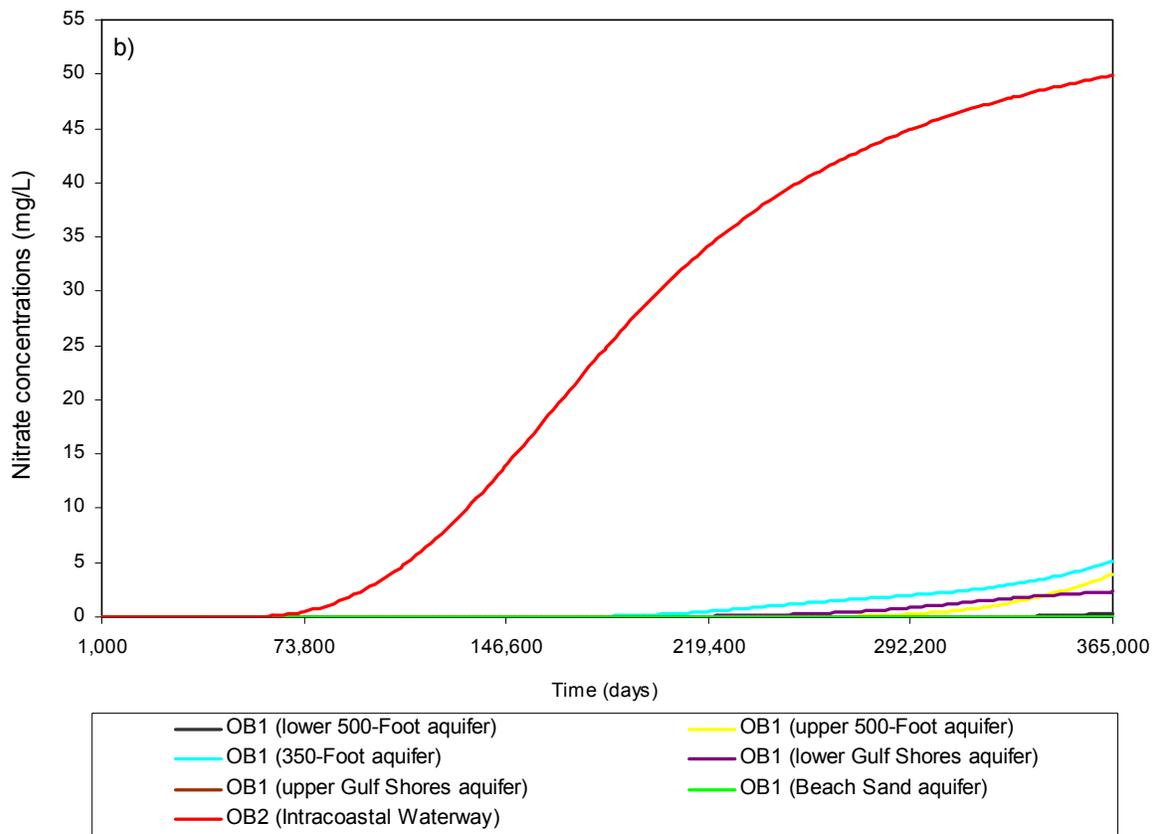
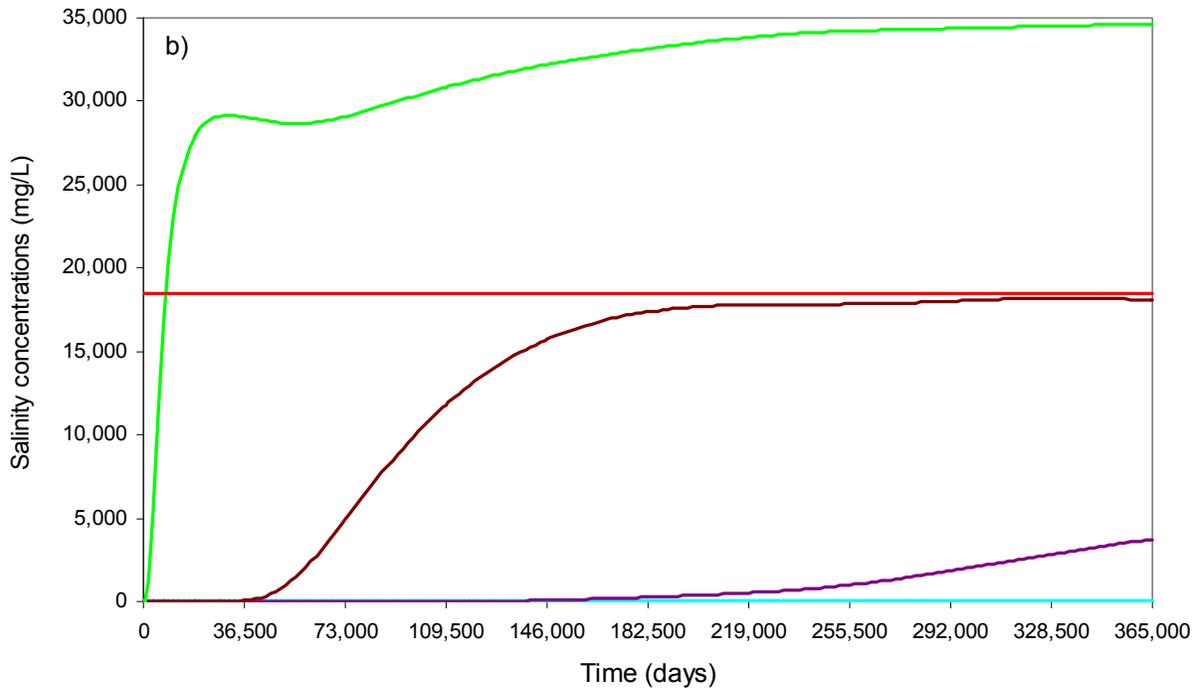
Under steady-state conditions, the one year calibration indicates no significant movement of the saltwater wedge. However, results of the 1,000 year transient simulation indicate that saltwater is moving into the upper two aquifers (Figs. 39, 40). Furthermore, the advancing rate is higher for the first 100 years when the assigned recharge does not reach the Intracoastal Waterway and the southern part of the model. The rate of seawater advancement into the lower Gulf Shores Aquifer and the 350-Foot Aquifer is very sensitive to the amount of flow coming from the North. Thus, the seawater front advances at a faster rate during the first part of the simulation and at a lower rate during the second part when the mound of water originating from northern recharge reaches the southern part of the model (Fig. 39). For the shallow, unconfined Beach Sand Aquifer, seawater advances northward, towards the Intracoastal Waterway at a relatively fast rate for the first 50 years (approximately 28,000 mg/L salinity after 50 years at the OB1 well) and then gradually increases to the seawater concentration towards the end of the simulation.



**Fig. 38** Generalized simulated hydrogeologic units, calibrated equipotential heads, and generalized flow paths



**Fig. 39** SEAWAT simulated nitrate and saltwater contaminant movement for four different time steps. Contour lines represent the location of the seawater wedge and nitrate front plume. Different colors are assigned for different time steps. Thinner lines represent the location of the nitrate front plume (nitrate concentrations equal to 5 mg/L) and thicker lines represent the location of the seawater wedge (salt concentrations equal to 250 mg/L)



**Fig. 40** Calculated salinity (a) and nitrate (b) concentrations recorded at wells OB1 and OB2

The variable-density simulation results reveal that nitrate discharge to the Gulf of Mexico from the shallow Beach Sand Aquifer and the semiconfined Gulf Shores Aquifer is minimized by the increased inland extent of the seawater front (Figs. 39, 40). The highest nitrate concentrations are recorded at the Intracoastal Waterway at observation well OB2 (Fig. 40). Minimum input of nitrate to the Gulf of Mexico comes from the deeper 500-Foot and shallow Beach Sand Aquifers whereas the maximum nitrate discharge originates from the 350-Foot Aquifer (Figs. 39, 40).

Nitrate movement within the aquifers underlying Southern Baldwin County and fluxes into the sea (i.e. Gulf of Mexico) by SGWD were examined using the computed velocity field and the nitrate concentrations in the aquifers near the shoreline at observation wells screened at six different depths (Figs. 36, 40). The simulated values of nitrate concentrations and flow pathlines were used to investigate the impact of surface water bodies on nitrate transport to the Gulf of Mexico. Calculated nitrate concentrations were observed at the Intracoastal Waterway (Fig. 34). Figures 38 and 40 depict the seaward nutrient fluxes caused by SGWD through the cross section at the Beach Sand Aquifer, the upper and lower Gulf Shores Aquifer, the 350-Foot Aquifer, and upper and lower 500-Foot Aquifers (e.g., OB1) (Fig. 36) and by Intracoastal Waterway discharge over the entire simulation period.

Nitrate migration rates are higher downward compared to those in the seaward direction (Fig. 39). Nitrate originating from the northern half of the model travels downward to the 350-Foot Aquifer and then migrates both vertically and horizontally. Therefore, nitrate in the deeper part of the aquifer system originates mainly from up-gradient sources. On the other hand, a larger degree of horizontal spreading was observed for the contaminant originating from sources located in the southern half of the model (Fig. 39). Consequently, nitrate originating from down-

gradient sources is more pervasive in the upper 350-Foot Aquifer. This behavior may be explained by the confining conditions of the aquifer system in the southern half of the model in contrast to the semiconfined to unconfined aquifer conditions in the northern half of the model domain (Fig. 33). Simulation results indicate that the first 50 to 100 years nitrate infiltrates as deep as 20 to 70 meters, respectively (Fig. 39). After 100 years, groundwater with initial nitrate concentrations equal to or exceeding 5 mg/L invades the 350 and 500-Foot Aquifers (Fig. 39) in the northern half of the area. Mixing of local sources in the absence of aquifer development is more likely to occur after 100 years from the beginning of the simulation (Fig. 39).

Groundwater flow velocities decrease in the vicinity of the coastline in the Beach Sand and Gulf Shores Aquifers due to the increased influx of seawater from the Gulf of Mexico to these aquifers (Figs. 39, 40). Groundwater velocities in the deeper 350 and 500-Foot Aquifers are generally constant. Thus, SGWD to the Gulf of Mexico is contributed by the 350 and 500-Foot Aquifers (Fig. 39). Nitrate flux to the Gulf of Mexico is dependent upon rates of SGWD and the severity of seawater influx to the aquifers. Thus, seaward nutrient fluxes caused by SGWD through the cross section are higher from the 350-Foot Aquifer and from the lower Gulf Shores and the upper 500-Foot Aquifers (Fig. 40). The lowest input of nitrate to the gulf comes from the shallow-unconfined Beach Sand Aquifer where seawater is moving inland at a faster rate compared to the deeper-confined aquifers. Although seawater intrusion occurs in the Gulf Shores Aquifer, nitrate discharges seaward through mixing and diffusion processes that take place within the transition zone. However, it was observed that nitrate fluxes to the Gulf of Mexico are higher from the lower Gulf Shores Aquifer. This difference is explained by the decreased groundwater velocity towards the coast within the upper Gulf Shores Aquifer and the resulting increased severity of seawater intrusion. For the deeper 500-Foot Aquifer, the seaward

nitrate flux occurs mainly through the upper portion. However, it should be noted that this is not because of lower SGWD through the lower 500-Foot Aquifer but rather the result of the timing of contaminant release from the source and travel times along flow paths.

Figures 39 and 40 show that Intracoastal Waterway canal discharge dominates nutrient supply to the Gulf of Mexico. The Intracoastal Waterway acts as a sink for the upper two most contaminated aquifers (Fig. 38, 40). Nitrate from shallow and deeper depths is being transported from the system through the Intracoastal Waterway. However, since waters from the canal discharge into Mobile Bay (Fig. 32), nitrate transported from the system will eventually, through an indirect path, discharge to the Gulf of Mexico. Therefore, because the canal receives a major part of nitrate from the upper two aquifers, groundwater contribution to the shallow water environment may be very low. Field observations conducted by Murgulet and Tick (2009a) revealed the presence of very low to absent nitrate and chlorophyll concentrations in surface water bodies located South of the Intracoastal Waterway. These observations are consistent with the model results, revealing the importance of the Intracoastal Waterway canal in removing nitrate from this area. Furthermore, the low nitrate concentrations observed in groundwater in the area South to the Intracoastal Waterway (Murgulet and Tick 2008) agrees with the simulation results. Nevertheless, local sources probably introduce some nutrient rich water directly into the near shore area.

#### Comparison of Nitrate Field Observation Data with SEAWAT Simulation Results

The calibrated flow model was used to simulate nitrate and seawater intrusion in the investigated aquifers along a general flow path. Initial nitrate concentrations assigned at the top layer were adjusted during several simulation scenarios in order to best match observed nitrate migration trends and concentrations. Simulation results indicate that nitrate input to groundwater

from the top of the water table can vary between 30 and 160 mg/L. The spatial extent of the nitrate for the first 100 years of the simulation is very similar to the 2006 and 2007 nitrate distribution observed by Murgulet and Tick (2008). Nitrate field measurements and calculated nitrate concentrations at wells shown in Fig. 35 are tabulated in Table 6. Although not calibrated for nitrate concentrations, the transport model results for the 100-year simulation time step indicate a reasonable good match with field observations (Table 6). The highest and lowest residual nitrate estimated based on the observed and calculated concentrations at each well were -6.1 and 11.6 mg/L. However, slightly subestimated values are more frequent (Table 6). This can be an indication of the presences of stresses caused by pumping which will force recently recharged waters with higher nitrate concentrations to greater depths. Since the model does not account for these stresses, this behavior is expected. The presence of higher measured nitrate concentrations at the observed depths can be explained by higher than simulated degrees of spreading of the contaminant in the investigated aquifer for the first 100 years. Nitrate concentrations of approximately 5 mg/L were recorded as deep as 100 m in the northern half of the study area. These results agree with the model simulations, indicating high vertical gradients for the top two aquifers (e.g. Figs. 39, 38). The presence of nitrate in concentrations higher than the background groundwater levels can be explained by the long-history of agricultural practices in this area. Both field observations and simulation results indicate that, once released from the different sources, nitrate migrates mainly vertically for the first approximately 100 years and slightly horizontally (Figs. 35, 39). Horizontal and vertical nitrate transport is enhanced by the processes of diffusion and dispersion. Mixing of different end member waters with different nitrate concentrations and residence times may enhance the processes of dilution or may contribute to locally increased nitrate concentrations at certain locations.

Table 6. Observed nitrate concentrations and calculated nitrate concentrations at the 100-year simulation time step, residual concentrations, and well field identification number

Well ID	Measured nitrate concentrations (mg/L)	Simulated nitrate concentrations (mg/L)	Residual (mg/L)
1	0.0	0.0	0.0
2	0.0	0.0	0.0
3	0.0	0.0	0.0
4	0.5	0.0	0.5
5	0.4	0.0	0.4
6	2.6	1.2	1.4
7	0.0	0.0	0.0
8	0.1	0.0	0.1
9	0.0	0.0	0.0
10	9.3	8.6	0.7
11	16.7	13.3	3.4
12	15.1	13.5	1.6
13	21.2	27.3	-6.1
14	1.9	0.0	1.9
15	80.8	69.2	11.6
16	63.4	55.8	7.6
17	0.1	0.0	0.1
18	0.0	0.0	0.0
19	0.2	0.0	0.2
20	0.1	0.0	0.1
21	47.2	47.9	-0.7
22	50.0	53.7	-3.7
23	3.2	3.4	-0.2
24	13.2	9.5	3.7
25	4.2	2.6	1.6
26	2.6	3.4	-0.8
27	21.4	13.8	7.6
28	37.7	41.2	-3.5
29	15.2	14.1	1.1
30	11.7	8.9	2.8
31	0.1	0.0	0.1
32	63.3	62.7	0.6
33	55.30	59.8	-4.5

Oxygen, hydrogen, carbon, and radiocarbon isotope investigations in combination with simulated flow paths in this area indicate the presence of high vertical gradients and low residence times, closely matching these observed contaminant trends (Figs 35, 39). Groundwater ages younger than 100 years were isolated mainly within these zones. Furthermore, the isotopic investigation of groundwater nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) conducted by Murgulet and Tick (2009a) indicates the existence of mixing patterns of several end-member waters with nitrate originating from various sources. Similarly, the model indicates that over a large period of time, mixing of up-gradient and down-gradient nitrate sources will likely occur (Fig. 39).

The transient model was also used to estimate the time it will take nitrate to be flushed out of the system if the contaminant source release was ceased after the first year of the simulation. Furthermore, this scenario is also useful in drawing conclusions about temporal changes in contaminant input. The results of this simulation indicate that under low recharge conditions, residual nitrate in concentrations of approximately 0.2 mg/L will still exist in the system after 200 years. Nitrate concentrations within the system are reduced due to processes of mixing, diffusion and dispersion. After roughly 300 years, nitrate in concentrations higher or equal to 0.2 mg/L is no longer present in the system. Nitrate removal from the system is not only due to the aforementioned processes but also due to discharge to the Intracoastal Waterway and diffusion to the freshwater/seawater transition zone. Nitrate discharge to the Gulf of Mexico through submarine groundwater discharge is less likely to occur since most of the nitrate plume is being diluted along the shallower flow paths. Hence, a permanent source of contaminant possesses the higher risk of contamination of coastal aquifers, surface waters, and to the Gulf of Mexico. In the presence of a continuous contaminant source, submarine groundwater discharge will play an important role in transporting contaminants to the Gulf of Mexico.

## Summary and Conclusions

In Southern Baldwin County, drought conditions, extensive agriculture and increased development are major factors that influence water quality and quantity and consequently freshwater availability. Nitrate and seawater contamination are two major water resources problems in this area. This study examined the influences of drought conditions, saltwater contamination, and surface-water levels on nitrate transport and discharge to the Gulf of Mexico. A two-dimensional (i.e. cross-sectional) model, incorporating regional geological, hydrological, geographical and topographic features was developed to aid in determining these effects. The model was calibrated to water-level data from 29 wells completed at various depths in the aquifer system in 2006, a period of severe drought and increased groundwater withdrawals. The simulated scenario is representative of steady-state conditions during a severe period of drought with minimum recharge and in the absence of pumping. The calibration parameters are derived from geophysical and driller's logs and from pumping tests. The variable density SEAWAT code was used to simulate the density-dependent flow and nitrate transport.

Simulation results reveal that nitrate and groundwater discharge to the Gulf of Mexico are minimized from the saltwater impacted aquifers. The Intracoastal Waterway has an important role in diverting groundwater from discharging into the Gulf of Mexico. Salinity concentrations recorded from the Intracoastal Waterway and the unnamed channel connecting Lake Shelby and Little Lagoon further suggest the dilution of water from the Intracoastal Waterway with fresh groundwater (e.g., 18,450 mg/L salinity) and that the unnamed channel is saltwater fed (e.g., 29,750 mg/L salinity). Therefore, nitrate outflow from the system occurs mainly through the Intracoastal Waterway and to a lesser extent through SGWD. Although, direct discharge of nitrate to the Gulf of Mexico through the cross section is minimized, a significant proportion of nitrate is likely transported to Mobile Bay and eventually to the Gulf of Mexico. The absence of

nitrate in groundwater and surface water in areas South of the Intracoastal Waterway (Murgulet and Tick 2008) is supported by the results of the model.

The variable-density groundwater flow and contaminant transport model indicates that the flow dynamics and contaminant transport processes within the aquifer system are additionally influenced by density variations that occur from the incursion of saltwater. Using the results of different simulated scenarios, residual nitrate concentrations in the saturated zone were estimated to range between 30 and 160 mg/L for the contamination source zones. Simulations results indicate that nitrate present in concentrations as high as 5 mg/L extend to the deeper Gulf Shores Aquifer (Aquifer A2). Travel times of nitrate to these depths range from modern to approximately 100 years. This is in relative agreement with the long history of agriculture and farming in this area. However, migration of nitrate at these depths may be the result of aquifer development and resulting increased vertical gradients as well as due to mixing, dispersion, and diffusion processes. The occurrence of high vertical gradients is revealed by simulated transport results, observed nitrate distribution along the simulated cross section, and by the radiocarbon data. The presence of nitrate at greater depth is accompanied by younger waters. For instance, groundwater ages ranging from modern to 100 years old were identified in areas where nitrate migrated vertically to the Gulf Shores Aquifer (Aquifer A2). At shallow depths nitrate exceeds concentrations greater than 80 mg/L. This suggests a permanent source of nitrate-contaminated modern water from the primary sources derived from the water table aquifer and the land surface.

Results of the different simulated scenarios indicate that if input of nitrate is ceased, after approximately 50 years, a residual nitrate in concentrations as low as 2 mg/L will be present at the top 50 meters of the aquifer. This concentration further decreases with increasing simulation

time. The size of the nitrate plume is increasing due to processes of dilution and diffusion while the concentration inside the plume is decreasing. However, even after 200 years, a residual nitrate concentration of approximately 0.2 mg/L will still exist in the southern part of the aquifer system. Residual nitrate in concentrations greater or equal to 0.2 mg/L will completely be flushed out of the system after 300 years. Therefore, in the absence of denitrification and a non-continuous contamination source, nitrate will persist in the system for long periods of time. Under these circumstances however, nitrate concentrations may be diminished by dilution and dispersion processes. Nevertheless, it should be mentioned that the time it takes a contaminant to be flushed out of the system and to be diluted is very much dependent on the amount of recharge that the system receives. It is suspected that greater dilution of the contaminant will occur during increased recharge conditions and therefore, shorter residence times within the aquifer system.

The SEAWAT model results reveal the importance of the Intracoastal Waterway in acting as a groundwater and contaminant sink for the Beach Sand and Gulf Shores Aquifers. The model predicts that the Beach Sand and Gulf Shores Aquifers will be impacted by severe saltwater intrusion, whereas the deeper 350 and 500-Foot Aquifers will experience negligible saltwater intrusion for the entire simulation period. This is primarily the result of preexisting elevated salinity concentrations and relatively low hydraulic head elevations in the close proximity to the coastline in the top two aquifers (e.g., the Beach Sand and Gulf Shores Aquifers) and the groundwater gradient reversal induced by the Intracoastal Waterway. Consequently, nitrate discharge to the Gulf of Mexico likely originates from the lower part of the aquifer system (e.g., the 350 and 500 Foot Aquifers) through submarine groundwater discharge. However, nitrate discharge to the Gulf of Mexico through the cross section from the upper Beach Sand and Gulf Shores Aquifers (A1 and A2) is not negligible. Nitrate discharges from these

aquifers through diffusion and seawater circulation within the seawater/freshwater transition zone. The Intracoastal Waterway acts as barrier to groundwater contaminant input to coastal waters located in the close proximity to the coast (e.g., Lake Shelby and Little Lagoon) by removing the largest part of nitrate from groundwater. However, significant nitrate discharge may occur to Mobile Bay from the Intracoastal Waterway.

Numerical simulations of nitrate transport indicate the degree to which a heterogeneous conceptual model can account for contaminant transport and dispersion relative to a conventional homogeneous model assuming typical dispersivity coefficients. The heterogeneous model transport results from this study are consistent with observed nitrate contamination patterns and depth distribution as well as depth-dependent groundwater-age trends. The model provides a realistic test-bed for prediction of future nitrate extent, including the time frame for potential nitrate impacts to deep wells, given that the geochemical data indicate that denitrification is not likely to occur.

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## OVERALL CONCLUSIONS

This is the first known study to model the complex dynamics of nitrate contamination and salt water intrusion using multiple characterization techniques. This research will serve as a tool which may be applied to other similar coastal systems for more effective management strategies. The complex approach to the nitrate and saltwater contamination problems may also contribute to further understanding of these groundwater and surface water systems allowing for an improved conceptual model of similar coastal systems.

Global fresh water resources are increasingly at risk due to severe overdraft and depletion of the supply, contamination of the supply, unsustainable population growth and development, and improper or lack of management. In particular, coastal aquifers worldwide are being severely stressed as a result of overpumping and related increases in aquifer vulnerability to contamination. Increased occurrence of problems such as saltwater intrusion in regional aquifers, increased flux of contaminants (i.e. nutrients, hydrocarbons, and inorganic species) to aquifers by anthropogenic activities have been recognized. The increased vulnerability to contamination also increases the potential of coastal water bodies (i.e. estuaries, wetlands, and the ocean) to be contaminated by discharging groundwater. For example, the Gulf of Mexico has recently experienced some of the largest hypoxic “dead zones” caused by widespread and persistent harmful algal blooms as a result of excessive anthropogenic nutrient loading. Groundwater and

surface water bodies in coastal regions throughout the world may be at higher risk of water resource depletion or degradation as many populations tend to concentrate around these desirable coastal regions. Comprehensive studies on regional and local groundwater flow dynamics, aquifer system evolution, and resulting effects on groundwater and surface water contamination in these coastal regions are critical for the development and implementation of appropriate water management strategies.

This dissertation integrates four different themes which are related through multiple comprehensive regional-scale studies of the aquifer system underlying Southern Baldwin County, Alabama. Specifically, the first theme of this dissertation examines the extent and magnitude of saltwater intrusion in order to elucidate important controls on the flux of saltwater inland from the Gulf of Mexico as well as vertical infiltration of saline water and the relative importance of mixing within the aquifer system. The second theme investigates contaminant source identification, fate, and transport within a coastal aquifer system. This study specifically focuses on the origin of nitrate and the primary processes controlling the transport and fate of nitrate within the aquifer system and its eventual discharge to coastal surface water bodies such as estuaries, wetland, and the Gulf of Mexico. The third major theme examines the groundwater flow dynamics and groundwater evolution through a coastal aquifer in order to determine the major processes controlling recharge, discharge, residence times, and mixing effects within the system and along major flow paths. The fourth theme investigates groundwater flow and transport dynamics in a coastal aquifer system implementing the use of a coupled variable-density groundwater flow and transport model. This modeling study was conducted to enhance the understanding of a coastal regional flow system by calibrating to observed hydraulic heads and comparing the results to what has been observed from the previous contaminant, multi-

isotope, geochemical, and saltwater studies as a part of this dissertation research. All four studies are conducted during a period of increased drought, reduced recharge, and increased aquifer development. The results of these studies reveal the impact of increased stress conditions in response to decreased recharge.

The results of this study indicate the presence of low salinity levels in the central and northern extent of the study area whereas elevated levels were observed in the local Aquifers A1 and A2 along the coastal areas adjacent to the Gulf of Mexico. Spatially extensive and persistent nitrate concentrations exceeding regulatory limits (MCL = 45 mg/L as nitrate) were identified within Aquifer A2 whereas only low nitrate concentrations were observed within the surficial Aquifer A1 and the deeper Aquifer A3. Nitrate was also absent in the investigated aquifers in area located South of the Intracoastal Waterway. The most extensive nitrate contamination is present in the central and northeastern portions of the study area. However, several other small regions throughout the study area exhibited elevated levels of nitrate. Surface water investigation studies revealed that Lake Shelby and Little Lagoon waters (located South of the Intracoastal Waterway) are not impacted by increased nitrate and chlorophyll concentrations. Conversely, Weeks Bay and Oyster Bay waters have a high degree of hypoxia due to the presence of elevated nitrate inputs and consequently increased algae growth and depleted oxygen levels. Analyses of nitrate and chloride data collected from the investigated aquifer system indicate that potential sources of nitrate in this area are fertilizer application and alternative sources such as sewer breakthrough and animal waste. Isotope analyses of groundwater nitrate and oxygen indicate that nitrate in groundwater is primarily derived from the nitrification of ammonium in soil from mixed sources such as fertilizer, sewer breakthrough, and manure application. Furthermore, isotope data indicate that denitrification was not an important process in this aquifer system. In

the absence of denitrification and the presence of a permanent source, it is expected that the elevated groundwater nitrate concentrations will not be readily attenuated posing a potential contamination and degradation problem of coastal discharge zones (i.e. wetlands, estuaries, lagoons, and coastal lakes) into the future. The narrow range of  $\delta D$  and  $\delta^{18}O$  values reflects the local meteoric origin of groundwater; that precipitation infiltrates rapidly to depth and does not undergo significant evaporation at the ground surface; any evaporation that may take place likely occurs before the precipitation water reaches the land. The range of values of  $\delta^{13}C$  data is indicative of a plant material signature (e.g., Hatch-Slack cycle). Therefore, groundwater in this area originates from locally infiltrated precipitation through soils extensively cultivated with plants such as corn, grass, and millet, which are widespread in temperate zones and in this area. Over the entire investigated area,  $\delta^{13}C$  values are nearly constant along the general north-South direction of groundwater flow and are similar for the investigated aquifers. This indicates that geochemical reactions such as carbonate dissolution that could increase the dissolved inorganic carbon content (DIC) concentration are not significant. Consequently, water in the aquifer system of the study area is most likely to have originated from precipitation and soil infiltration through relatively localized recharge.

The radiocarbon data indicate that waters in deeper Aquifers A2 and A3 have been recharged beginning in the early Holocene. However, middle and late Holocene recharge waters are pervasive in the aquifer system of Southern Baldwin County. The  $\delta^{13}C$ ,  $\delta^{18}O$ ,  $\delta D$ , and  $^{14}C$  isotope data, indicate the existence of multiple recharge areas within the region and mixing of source waters with ambient waters during transport (due to naturally occurring and induced gradients). The relationship between  $\delta^{18}O$  and  $A^{14}C$  values suggests that locally derived groundwater with high  $^{14}C$  content mixes continually along flow paths with lower  $^{14}C$  ambient

groundwater. The data further suggests that high vertical gradients and recharge rates are likely due to the nature of the permeable sediments and potentially to increased gradients as a result of significant pumping. Therefore, the presence of short residence times and the absence of denitrification processes, indicate the oxic character of the investigated system. These isotope studies support the hypothesis that the aquifer system in Southern Baldwin County is a highly dynamic system experiencing mixing of recent recharged waters with older, ambient groundwaters in response to increase stresses as a result of reduced recharge. Furthermore, isotope data and recharge area distribution analyses indicate the increased vulnerability to contamination of these highly developed aquifers

The variable-density groundwater flow and contaminant transport model indicates that the flow dynamics and contaminant transport processes within the aquifer system are additionally influenced by density variations that occur from the incursion of saltwater. Using the results of different simulated scenarios, residual nitrate concentrations in the saturated zone were estimated to range between (lower to higher 30 to 160 mg/L) for the contamination source zones. Simulations results indicate that nitrate present in concentrations as high as 5 mg/L extend to the deeper Gulf Shores Aquifer (Aquifer A2). Travel times of nitrate to these depths ranges from modern (0 to 50 years) to approximately 100 years. This is in relative agreement with the long history of agriculture and farming in this area. However, migration of nitrate at these depths may be the result of aquifer development and resulting increased vertical gradients as well as due to mixing, dispersion, and diffusion processes. Even though not calibrated for concentrations, simulated nitrate transport reveals similar migration trends and concentration distribution with those observed from field data. The occurrence of high vertical gradients is revealed by simulated transport results, observed nitrate distribution along the simulated cross section, and by

the radiocarbon data. The presence of nitrate at greater depth is accompanied by younger waters. For instance, groundwater ages ranging from modern to 100 years old were identified in areas where nitrate migrated vertically to the Gulf Shores Aquifer (Aquifer A2). At shallow depths nitrate exceeds concentrations as high as 80 mg/L. This is an indication of a permanent source of nitrate contaminated modern water from the primary sources derived from the water table aquifer and the land surface.

Results of the different simulated scenarios indicate that if input of nitrate is ceased, after approximately 50 years nitrate will no longer be present in the top 50 meters of the aquifer. Furthermore, a residual nitrate concentration of approximately 0.2 mg/L will still exist in the southern part of the system even after 200 years. Residual nitrate will be completely flushed out of the system after 300 years. Therefore, in the absence of denitrification and a non-continuous contamination source, nitrate will persist in the system for long periods of time. Under this circumstances however, nitrate concentrations seem to be diminished by dilution and dispersion processes.

The SEAWAT model results reveal the importance of the Intracoastal Waterway in acting as a groundwater and contaminant sink for the Beach Sand and Gulf Shores Aquifers. The model predicts that the Beach Sand and Gulf Shores Aquifers will be impacted by severe saltwater intrusion whereas the deeper 350 and 500-Foot Aquifers will experience no saltwater intrusion for the entire 1,000-year simulation period. This is mainly the result of already existing elevated salinity concentrations and low head elevations in close proximity to the coastline in the top two aquifers (e.g. the Beach Sand and Gulf Shores Aquifers) and the groundwater reverse gradient induced by the Intracoastal Waterway. Consequently, nitrate discharge to the Gulf of Mexico originates from the lower part of the aquifer system (e.g. the 350 and 500 Foot Aquifers)

through submarine groundwater discharge. However, nitrate discharge to the Gulf of Mexico through the cross section from the upper Beach Sand and Gulf Shores Aquifers (A1 and A2) is not negligible. Nitrate discharges from these aquifers through diffusion and seawater circulation within the seawater/freshwater transition zone. The Intracoastal Waterway acts as barrier to groundwater contaminant input to coastal waters located in the close proximity to the coast (e.g. Lake Shelby and Little Lagoon) by removing the largest part of nitrate from groundwater.

The hydrological and geochemical data collected for the purpose of this study is representative of a highly dynamic system, which may be the result of both decreased recharge rates and resulting increased stresses as the result of overdevelopment of groundwater resources (e.g. pumping). In both situations, high vertical gradients are characteristic in a highly permeable aquifer system. Although the variable density model does not account for stresses such as pumping, it further reveals the presence of high vertical gradients and the increased vulnerability to contamination of the deeper aquifers.

Integration of geochemical, isotopic, geological, hydrogeological, geographic GIS, land-use land-cover, and numerical modeling techniques help create a framework of the current status of groundwater and surface water interactions and contaminant sources and transport.

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