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Geochemical Evidence for Vertical Migration of Deep Formation Fluids through the Baton Rouge -Denham Springs Fault System

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Geochemical Evidence for Vertical Migration of Deep Formation Fluids through the
Baton Rouge -Denham Springs Fault System

A Thesis

Submitted to the Graduate Faculty of the
University of New Orleans
in partial fulfillment of the
requirements for the degree of

Master of Science
in
Earth and Environmental Sciences
Geology

by

Lesley Cady Prochaska

B.S. University of New Orleans, 2000

December, 2012

Dedication

To those in my life whether a small part or center stage, your role made the composition of who I am thank you. My daughter Emeline, thank you for being the motivation to follow my dreams.

Acknowledgements

I would like to express my sincere thanks to my thesis committee chair, Professor Emeritus Dr. Ronald Stoessell, for his guidance, support, and belief in second chances. Wind, rain, fire, nor hurricane Katrina could put asunder what we started. Also thank you to Dan Tomaszewski of the US Geological Survey, for sharing resources and access to the groundwater monitoring well network.

I acknowledge the cooperation of the thesis committee members who kept the flame alive: Professor Dale Easley and Professor Mark Kulp.

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Abstract

Accumulations of brackish groundwater exist across south Louisiana within the shallow, south-dipping Pleistocene to Upper Miocene Baton Rouge Aquifer System (BRAS). This research investigates the source of brackish groundwater through geochemical analysis of representative groundwater samples by comparing the following geochemical ratios along with other trace elements. Low Bromide (Br)/Chloride (Cl) and Potassium (K) /Cl ratios, high Sodium (Na) /Cl ratios, trace Magnesium (Mg) concentrations, and low Strontium (Sr) $^{87}\text{Sr}/^{86}\text{Sr}$ in brackish waters from the BRAS are inconsistent with *in situ* saline water from marine formation fluids of similar age. The ratios are consistent with *in situ* saline-water sources from Lower Miocene or Paleogene formation fluids from dissolved recrystallized halite. Deep formation fluids have interacted with Louann Salt diapirs underlying the BRAS area, dissolving halite, and are shown to have moved up fault planes and entered shallow aquifers to mix with the *in situ* groundwaters.

Keywords: Geochemistry, Baton Rouge Aquifer, Baton Rouge-Denham Springs Fault System, Halite, Strontium, Brackish, Groundwater, Louann Salt, Diapirs, Faults, Geochemical Ratios

Introduction

Local accumulations of brackish groundwater occur across south Louisiana within the shallow south-dipping Pleistocene, Pliocene and Upper Miocene formations in the BRAS. The purpose of this study was to chemically fingerprint the saltwater sources of brackish groundwaters in shallow BRAS and to determine if these were *in situ* down dip marine pore waters or from deeper marine formation fluids that have an increased salinity due to halite dissolution. The study is part of ongoing research that is analyzing groundwater from locations throughout the entire southern Louisiana aquifer system (Stoessell 1997; Stoessell and Prochaska, 2005).

While this study's initial intent was to examine only the BRAS, its scope was expanded to include groundwater from two additional areas in southern Louisiana. The additional areas included were St. Tammany Parish and coastal Louisiana parishes (Figure 1). The expansion of the study area was included in this research to provide a more in-depth view of the entire South Louisiana Aquifer System brackish waters. Overall results from South Louisiana have previously been published in Stoessell and Prochaska (2005).

Significance

The BRAS provides drinking water for more than 400,000 people in East Baton Rouge Parish alone (Sargent, 2007) and used for industrial, agricultural and domestic purposes. For example, in 2005 East Baton Rouge Parish used approximately 28 million gallons per day (mg/d) from the 2,800-foot sand in which 9.2 mg/d was used for public supply and 18.8 mg/d was for industrial use (Fendick, 2007). In the second quarter of 2006, groundwater withdrawals from the aquifer system in East Baton Rouge Parish totaled 191 mg/d (Capital Area Ground Water Conservation Commission, 2006). Prior to development, fresh water flowed south to the Baton Rouge-Denhim Spring (BR-DS) fault system, an east-west trending growth fault that extends through Baton Rouge and across southeastern Louisiana. Aquifers south of the fault generally contained saltwater

(Figure 2). The large withdrawals in East Baton Rouge Parish due to development have lowered water levels and altered flow patterns in most of the 10 aquifers that underlie the area (Lovelace, 2007). Groundwater withdrawals north of the fault have created gradients favorable for the movement of saltwater from south of the fault into fresh water areas north of the fault. The continued northward movement of the fresh water/ brackish water boundary in the aquifers has been documented by the US Geological Survey. On the basis of current trends, the future sustainability of the BRAS to provide drinking water that meets US Environmental Protection Agency's Office of Ground Water and Drinking Water standards is brought into question. In order to accurately implement strategies to address the issue, the geologic framework and the sources of saltwater need to be understood.

Applied Considerations

Although the number may be disputed by the agencies involved, the population of the city of Baton Rouge has increased significantly since Hurricane Katrina in August 2005. According to the Baton Rouge Area Chamber, the population estimate of the Baton Rouge Metropolitan Statistical Area encompassing Ascension, East Baton Rouge, East Feliciana, Iberville, Livingston, Point Coupee, St. Helena, West Baton Rouge, and West Feliciana parishes pre-Hurricane Katrina was 729,000 persons (Baton Rouge Area Chamber, 2008). The Chamber's post-Hurricane Katrina 2006 population estimate was 779,000, which is a 10 percent increase in population from 2000 to 2006. With the current and projected population increase comes an increased demand for water. Now is the time to look ahead 20 or 30 years to see what the projected water needs will be. In addition to understanding the BRAS hydrogeology, alternatives for drinking water sources also need to be investigated. Desalination is a possibility in areas where the aquifers contain brackish water. Economically, desalination of brackish water is cheaper than it is for saltier seawater (e.g. Tampa Bay). A variation of desalination is the use of scavenger wells, where fresh and saltwater are pumped simultaneously and

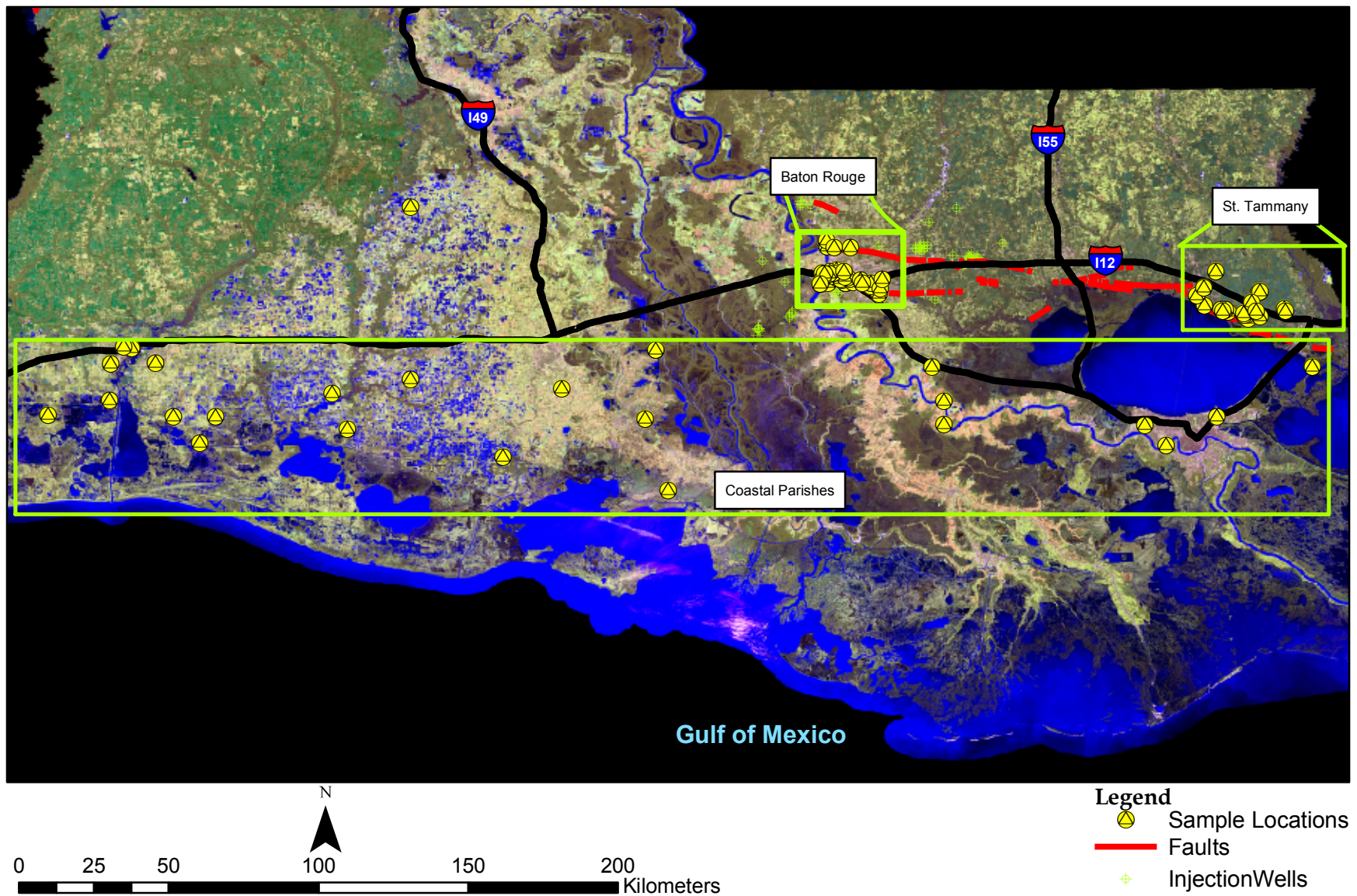


Figure 1: Study area and sample locations used to determine if the source of brackish groundwaters are in *in situ* down dip marine pore waters or from deeper marine formation fluids (modified from LDEQ, 2002).

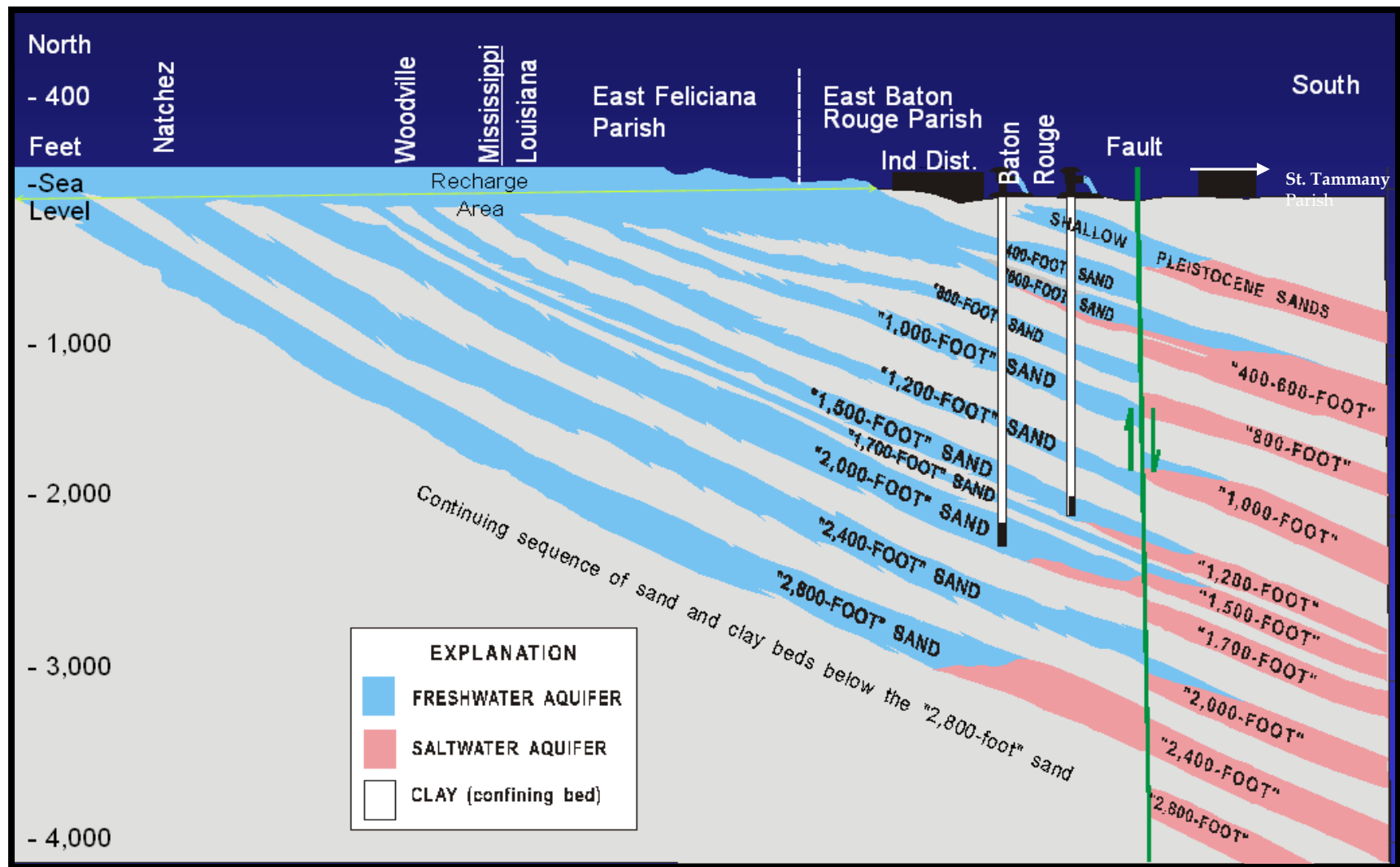


Figure 2: Idealized cross-section of Baton Rouge Aquifer System showing fresh water and saltwater locations. Most previous researchers have assumed the source of the salt water to be in situ diagenetically-modified sea water in the downdip aquifers, crossing the fault and migrating updip (modified from USGS, 2002).

the saltwater dumped. The future water needs of Baton Rouge will possibly be a combination of sources and strategies. For example, a source for drinking water that would reduce the demand on the BRAS is surface water. A nearby source to the east of the Baton Rouge area of good quality surface water is the Amite-Comite River system. The system has an advantage over the Mississippi River due to low hardness and dissolved solids as well as clarity. The Comite River Diversion Canal should be completed by 2018 (Amite River Basin Commission, 2012). The impoundment will have a storage capacity of billions of gallons of good quality water that has potential to be utilized for drinking water.

Theoretical Considerations

In addition to understanding the geologic framework to thwart the northward movement of the fresh water/brackish groundwater boundary, other potential implications are brought into consideration with evidence of vertical movement of deep formation fluids into shallow groundwater aquifers. The use of injection wells for disposal below the Baton Rouge Aquifer System is one because these are commonly used for wastewater disposal. If saltwater movement occurs vertically up the fault, this calls into question the isolation of wastewaters in deep-well injections below the aquifer system and the potential for contamination of the drinking water aquifers from injection well wastewater moving up the BR-DS fault system (Figure 3).

Evidence of vertical movement of deep formation fluids into shallow groundwater aquifers, possibly along fault lines, brings into conjecture that significant groundwater withdrawal changed the BR-DS fault system hydrogeology, contributing to fault movement and subsequent subsidence in southern Louisiana. For example, the industrialized area under the Exxon Refinery in North Baton Rouge along the Mississippi River north of the BR-DS fault system has subsided 1.67 feet in the last 41 years (Louisiana Geological Survey, 2001).

Southern Louisiana's area subsidence problem has been attributed in part to fault movement. The prevailing theory is that subsidence is a result of young sediment causing low lying compaction/consolidation predominantly affecting shallow soils (Dokka, 2006). However, current research supports the contrary that up to 50 percent of subsidence in the area is caused by fault movement. Subsidence associated with fault movement also impacts deeper soils instead of being limited to shallow soils (Dokka, 2006). The change in the theory may be partially attributed to renewed motion along some Louisiana southern fault lines. Some researchers consider the fault creep in the area to be human-induced and related to groundwater withdrawal (Holzer and Gabrysch, 1987).

Background

The surface of Louisiana is underlain by sedimentary sequences that were deposited in or adjacent to rivers and deltas in a coastal-plain setting. The sequence of sedimentary layers dips toward the Gulf of Mexico. These deposits indicate that a major river system corresponding to the Mississippi has persisted at least since the Gulf of Mexico began to form by the separation of North America from South America during the Triassic time period (Mann and Thomas, 1968). The history of the Gulf of Mexico began when Pangaea started to rift creating a seawater filled basin between North and South America. The evaporation of seawater between the two continents left behind thick layers of evaporate minerals, such as salt, anhydrite, and gypsum. These salt deposits from the Triassic and Jurassic Periods are known as the Louann Salt (Salvador, 1987). During the Cretaceous Period the layers of sediments were deposited into the Gulf over the Louann salt (Figure 4). Today, the Louann Salt deposits are

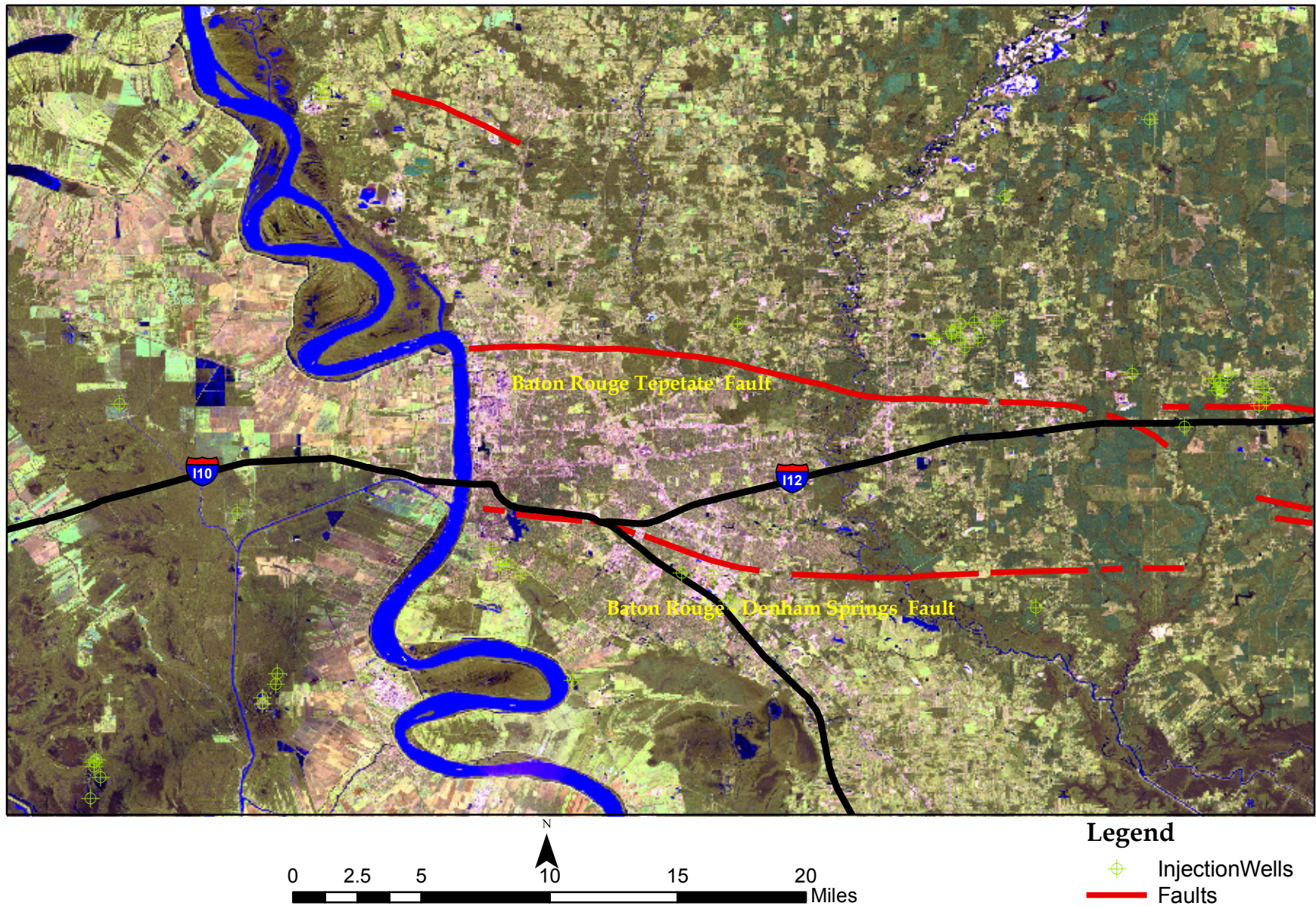


Figure 3: Baton Rouge Fault System and proximity of injection well locations in which the isolation of wastewaters

buried 20,000 to 30,000 feet (ft) beneath Louisiana's surface (Barton, 1933). The salt flows under pressure, deforming the overlying strata and forming salt domes. Louisiana Salt domes are distributed underneath the whole of Louisiana. High rates of subsidence, sedimentation, and salt migration have produced faults, folds, and inter-fingered strata.

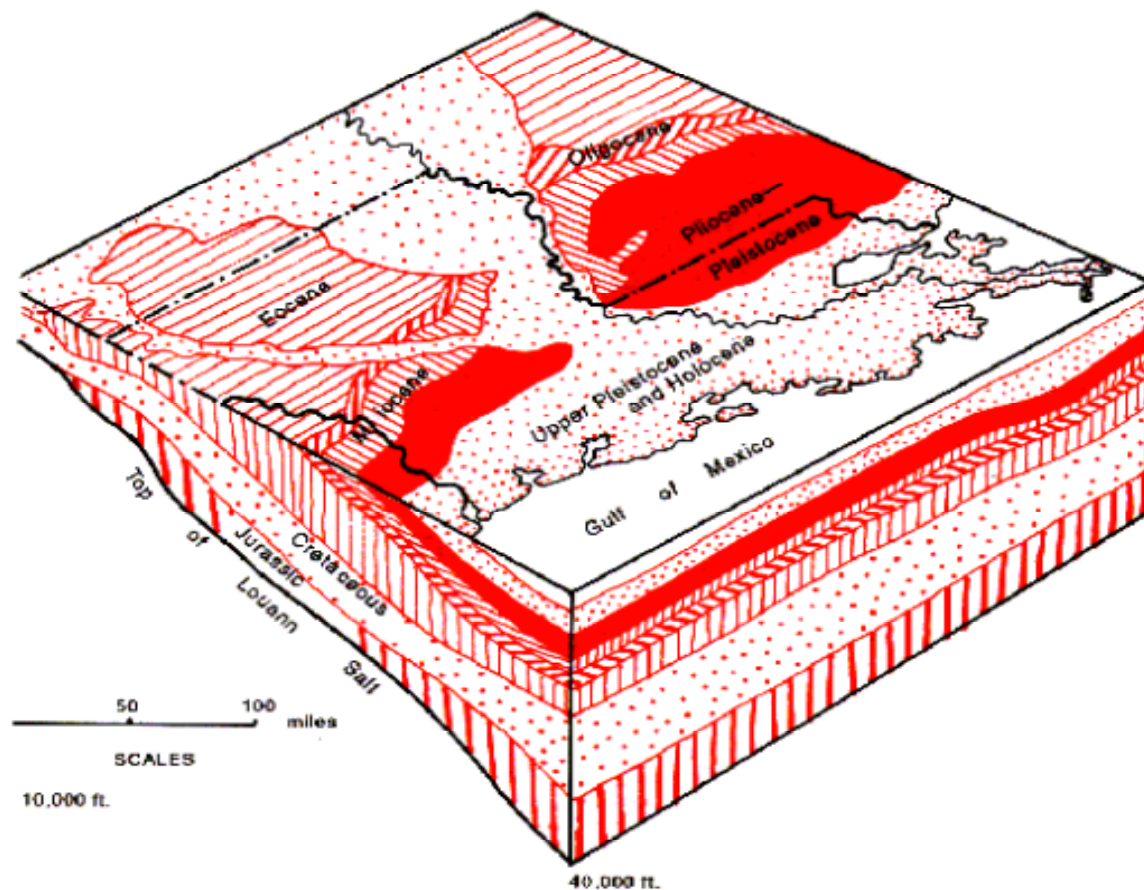


Figure 4 Subsurface stratigraphy and structure of Louisiana from Pleistocene to Jurassic (from Spearings, 1995).

The groundwater resources of Louisiana are stored in inter-fingered strata ranging from the Eocene Wilcox aquifer in northern Louisiana to the Holocene alluvial aquifers found along the Mississippi and Red rivers. Four primary aquifer systems are

found in the state: the Southern Hills in the southeast, the Chicot in the southwest, the Sparta in the northwest, and the Mississippi River Alluvial in the northeast. The Chicot and Southern Hills aquifer systems of southern Louisiana contain a majority of the state's potable groundwater. However, the majority of groundwater used in Louisiana is from Pleistocene sands within the Chicot and Mississippi River Alluvial aquifer systems (Louisiana Geological Survey (LGS), 2008).

Baton Rouge Area (East and West Baton Rouge Parishes)

East and West Baton Rouge Parishes are in southeastern Louisiana, and are located on the east and west side, respectively, of the Mississippi River. Eastern East Baton Rouge Parish surface soils consist of loess-like soils with high silt content deposited by aeolian process. The remaining area surface soils were developed from sands, silts, and clays deposited by the Mississippi River (United States Department of Agriculture, (USDA), 1968a). The surface soil is underlain by coast-parallel terraces formed by deposits of the Mississippi River and smaller coastal-plain streams from the recent geologic past, and these elevated terraces are incised by the bottomlands of the river and streams, in which sediment is still being deposited today. The Prairie Terrace is exposed over most of East and West Baton Rouge Parishes and broken by the BR-DS and the Baton Rouge-Tepetate Fault Systems, which are collectively referred to as the Baton Rouge Fault System (LGS, 2001).

Aquifer System

The Louisiana Geological Survey (Snead and McCulloh, 1984) reports the BRAS consists of shallow, south-dipping Pleistocene alluvial and terrace deposits and Pliocene and Upper Miocene sand aquifers. It is one of three aquifer systems that comprise the Southern Hills hydraulic system that also includes the St. Tammany and the Florida Parishes. The Pleistocene alluvial aquifers are moderately to well sorted with fine sand near the top grading to coarse sand and gravel in the lower parts. Layers of silt and clay act as confining units. The Pliocene aquifers consist of moderately to well sorted fine to medium grained sands interbedded with coarse sand, silt, and clays. The Miocene aquifers are fine to coarse sand and gravel. The sand aquifers are confined by clay units and were deposited in deltaic sequences with marine pore waters. The aquifers are cut by the Baton Rouge Fault System, the two south dipping, east-west trending gravity faults (Figure 5) and overlie the deep, Jurassic Louann Salt deposits, which are the source of the salt diapirs in South Louisiana (Ewing and Lopez, 1991.) The Baton Rouge Fault System extends eastward from Baton Rouge for 100 miles (160 km) across southeast Louisiana (Figure 3) and reaches a depth of more than 6 km (Lopez et al., 2002). The up-thrown north side of the Baton Rouge – Denham Springs Fault is predominantly fresh water and the down-thrown south side is thought to be predominantly brackish water.

The aquifer sands in the Baton Rouge Industrial area in East Baton Rouge were identified and named for their approximate depth of deposition by Meyer and Turcan (1955), the 400, 600, 800, 1,000, 1,200, 1,500, 1,700, 2,000, 2,400, and 2,800 ft sands (Table

1). Aquifer nomenclature varies in East and West Baton Rouge and surrounding parishes (Halford and Lovelace, 1994). The 400 and 600 ft aquifers are Chicot equivalent aquifer system and produce large volumes of water typically moderately hard to very hard calcium carbonate type water. The 800, 1000, 1200, 1500 and 1700 ft sand aquifers are Evangeline equivalent aquifer system and also produce large amounts of water. The 1200 ft aquifer is the most important because it has little brackish water.

Where the Evangeline equivalent sand aquifers are connected to the alluvial aquifers, the water produced is chemically similar. However, as the water moves toward the Mississippi syncline, it is modified to a soft, sodium bicarbonate type of water. The 2,000, 2,400 and 2,800 ft aquifer sands are Jasper equivalent aquifer system containing soft, alkaline, and of the sodium bicarbonate type water (USDA, 1968b). The 1,500, 2,000, and 2,800 ft sands are the most heavily pumped aquifers in the Baton Rouge area (Tomaszewski, 1996). The aquifers have different ranges of transmissivity, thickness, and storage coefficient (Table 1). The major clay units between the aquifers range from less than 1 ft to 100 ft in thickness over the greater Baton Rouge area (Bear 1979; Halford and Lovelace, 1994). Aquifers are hydraulically connected by leakage through clay layers and some aquifers merge locally. The hydraulic conductivity of clay units ranges from 3×10^{-8} to 0.3 ft/d (Bear, 1979; Halford and Lovelace, 1994). The vertical hydraulic conductivity of clay units based on laboratory analysis of some samples collected from the industrial area at a depth of 447 to 455 ft is 0.000011 ft/ft. Samples taken at a depth of 2,113 to 2,116 ft yielded the value of 0.000016 ft/ft (Whiteman, 1980, Halford and Lovelace, 1994). The confining units found in the East

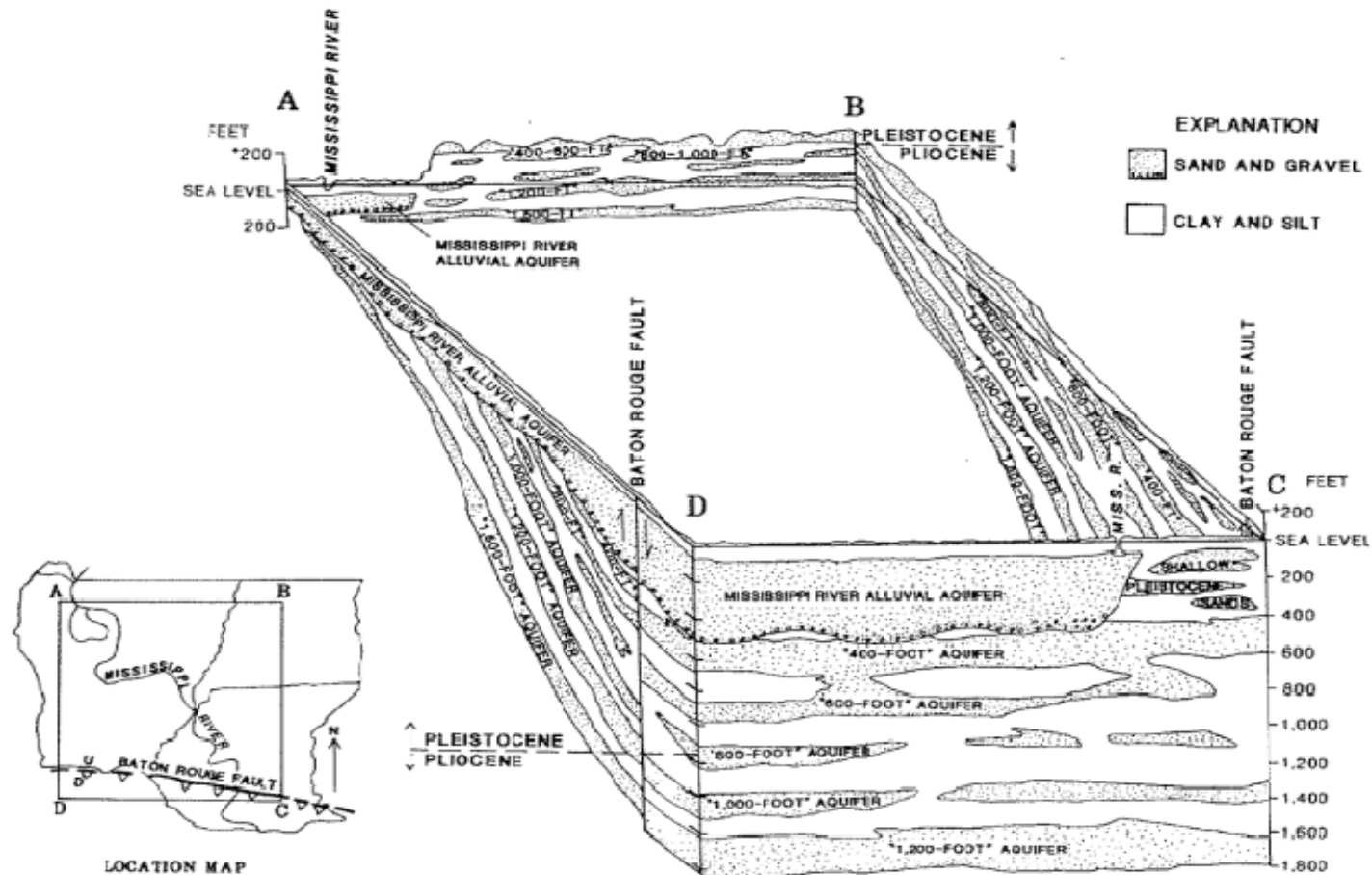


Figure 5 Generalized fence diagram of the Baton Rouge Aquifer System in relationship to the south dipping, east-west trending Baton Rouge-Denham Springs Fault System (from Kuniansky et al., 1989).

Table 1 Louisiana southern aquifer system lithology and nomenclature (modified from Lovelace and Lovelace, 1995).

System	Series	Stratigraphic Unit	Aquifer System or Confining Unit	Baton Rouge Area Aquifers	Lithologic Description	Transmissivity in ft ² per day	Thickness in feet	Coastal Parishes			St. Tammany Parish Aquifers
								Lake Charles Area Aquifers	South Central LA Aquifers	New Orleans-Gonzales Area Aquifers	
Quaternary	Holocene	Mississippi River, alluvial deposits	Near-surface aquifers	Mississippi River alluvial aquifer				Shallow sand 200-ft sand	Shallow sand	Shallow sand	Upland Terraces
	Pleistocene	Terraces Prairie Montgomery	Chicot Equivalent aquifer system	Shallow sand "400-ft" sand "600-ft" sand	Fine sand to pea gravel	1,400-26,000	75 - 400	500-ft sand 700-ft sand	Upper Chicot Lower Chicot	Gramercy Norco-Gonzales New Orleans 1,200-ft sand	Upper Ponchatoula
Upper Neogene	Pliocene	Blounts Creek Member	Evangeline Equivalent aquifer system	"800-ft" sand	Fine to medium sand	3,400	50-150				Lower Ponchatoula
				"1,00-ft" sand	Fine to coarse sand	9,500	40-90				
				"1,200-ft" sand		10,000 -17,00	40-100				Big Branch
				"1,500-ft" sand	Fine to medium sand	4,300 - 12,000	200-300				Kentwood-Abita
	Upper Miocene	Williamson Creek , Dough Hills, Carnahan Bayou	Jasper Equivalent aquifer system	"1,700-ft" sand							Covington/Sli dell
				"2,000-ft" sand	Medium sand	22,000 - 39,000	100-300				Tchefunta
				"2,400-ft" sand	Fine to Medium sand	13,000	50-250				Hammond
				"2,800-ft" sand	Fine to coarse sand	17,000	50-350				Amite

ft² = feet squared

Source: modified from Lovelace and Lovelace (1995)

and West Baton Rouge Parish area contain considerable amounts of silt and sand. The overall hydraulic conductivity is more likely about 0.0005 ft/d (Halford and Lovelace, 1994).

Brackish Water Encroachment

Large withdrawals from the Baton Rouge area have lowered water levels and altered flow patterns in most of the BRAS (Tomaszewski, 1996). Prior to development, fresh water flowed south to the BR-DS Fault and aquifers south of the fault system generally contained saltwater. Saltwater encroachment was first detected north of the updip side of the fault system in the 600 ft sand in 1948 in well EB-123 which is 0.5 mile north of the BR-DS Fault and four miles south of the center of pumping from the 400 ft and 600 ft sands (Meyer and Turcan, 1955). Since 1955, saltwater encroachment also has been documented in the 800, 1,000, 1,500, and 2,000 ft sands underlying the BRAS (Morgan and Winner, 1964; Whiteman, 1979; Tomaszewski, 1996). These studies also documented the presence, but not encroachment, of saltwater in the 400, 1,200, and 2,800 ft sands north of the BR-DS Fault System. Researchers working on saltwater intrusion in the Baton Rouge area have generally assumed that downdip *in situ* marine pore waters were moving northward (updip) within the aquifers and crossing the BR-DS Fault in response to fresh water removal exceeding surface recharge (e.g., Rollo, 1969; Whiteman, 1979). Saltwater movement north of the fault per the US Geological Survey is affected by aquifer permeability, depressions, or ridges in the base of the aquifer, and the slope of the base of the aquifer (Tomaszewski, 1996). Hydraulic gradients, which are affected by withdrawals in the study area, also affect the direction and rate of saltwater movement.

Most of the shallow Baton Rouge sand aquifers from 400 to 2,800 ft sands currently contain some brackish waters updip (north) of the BR-DS fault system as shown on Figure 6 based on USGS data from 1992 (Tomaszewski, 1996). The two most heavily pumped aquifers with the saltwater front near the fault are the 1,500 and 2,000 ft sands in which the front is moving northward, respectively, at estimated rates of about 100 ft/yr. Displacement of the aquifers near the fault was assumed to act as a partial barrier to the fluid movement. The Pliocene and Upper Miocene aquifers south of the fault are thought to contain primarily saltwater; however, the limited available water-quality data does not preclude occurrences of fresh water in these aquifers south of the fault.

The Capital Area Ground Water Conservation Commission (CAGWCC) and US Geological Survey entered into an agreement in 2004 to 2005 and subsequent extension in 2006 to do an extensive chloride sampling project in East and West Baton Rouge to monitor saltwater encroachment. One hundred and fifty two wells were sampled. The background concentration for chloride in fresh groundwater in the Baton Rouge area north of the Baton Rouge fault is generally less than 10 mg/L. Twenty-three groundwater samples exceeded background including several wells that had not previously exceeded background. Chloride concentrations exceeded background in one or more samples from wells north of the BR-DS Fault in nearly all the shallow groundwater zones. Comparison of the 2004 through 2005 data with historical data indicated that chloride concentrations are increasing at wells in seven of the aquifers

600, 1,000, 1,200, 1,500, 2,000, 2,400, and 2,800 ft sands north of the Baton Rouge fault (Lovelace, 2007).

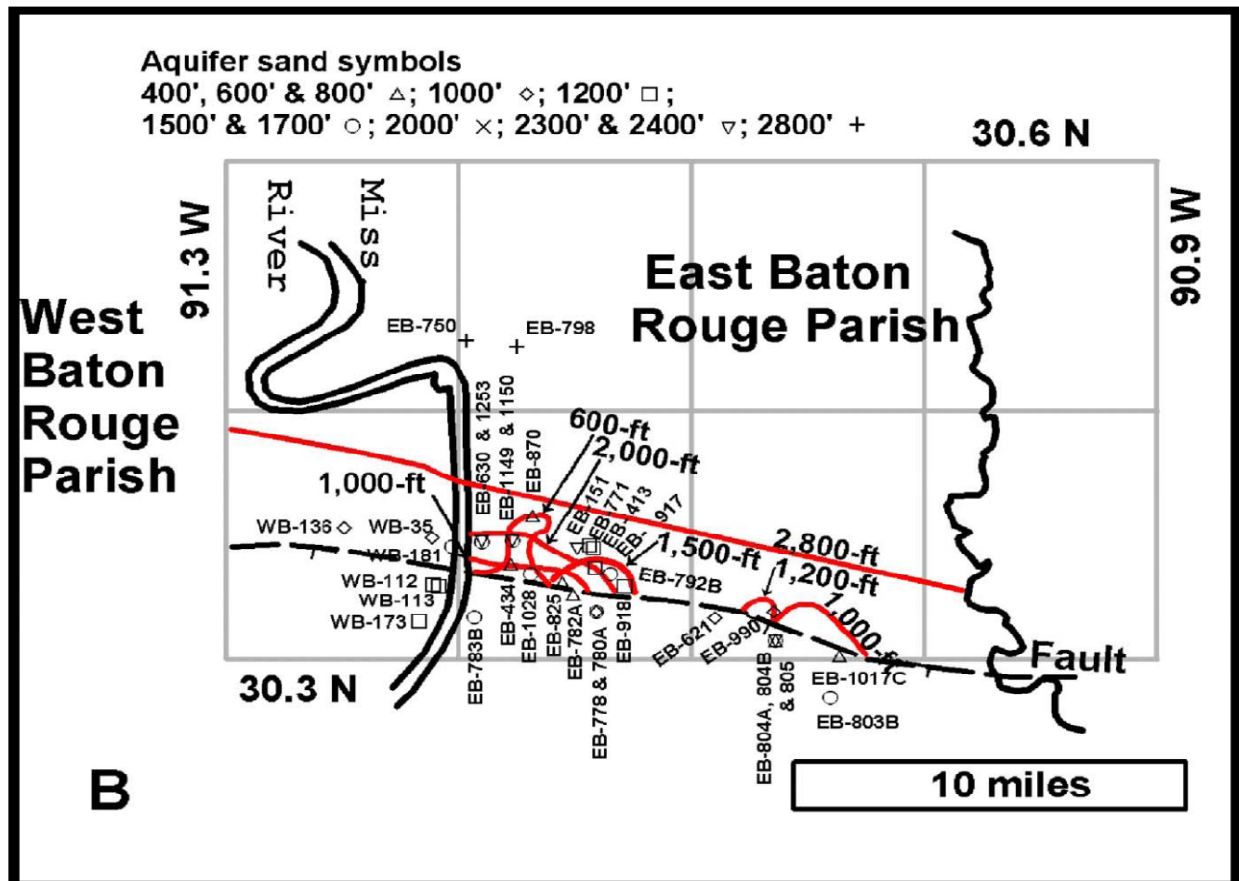


Figure 6 Baton Rouge Aquifer System 1992 saltwater fronts (modified from Stoessell and Prochaska, 2005).

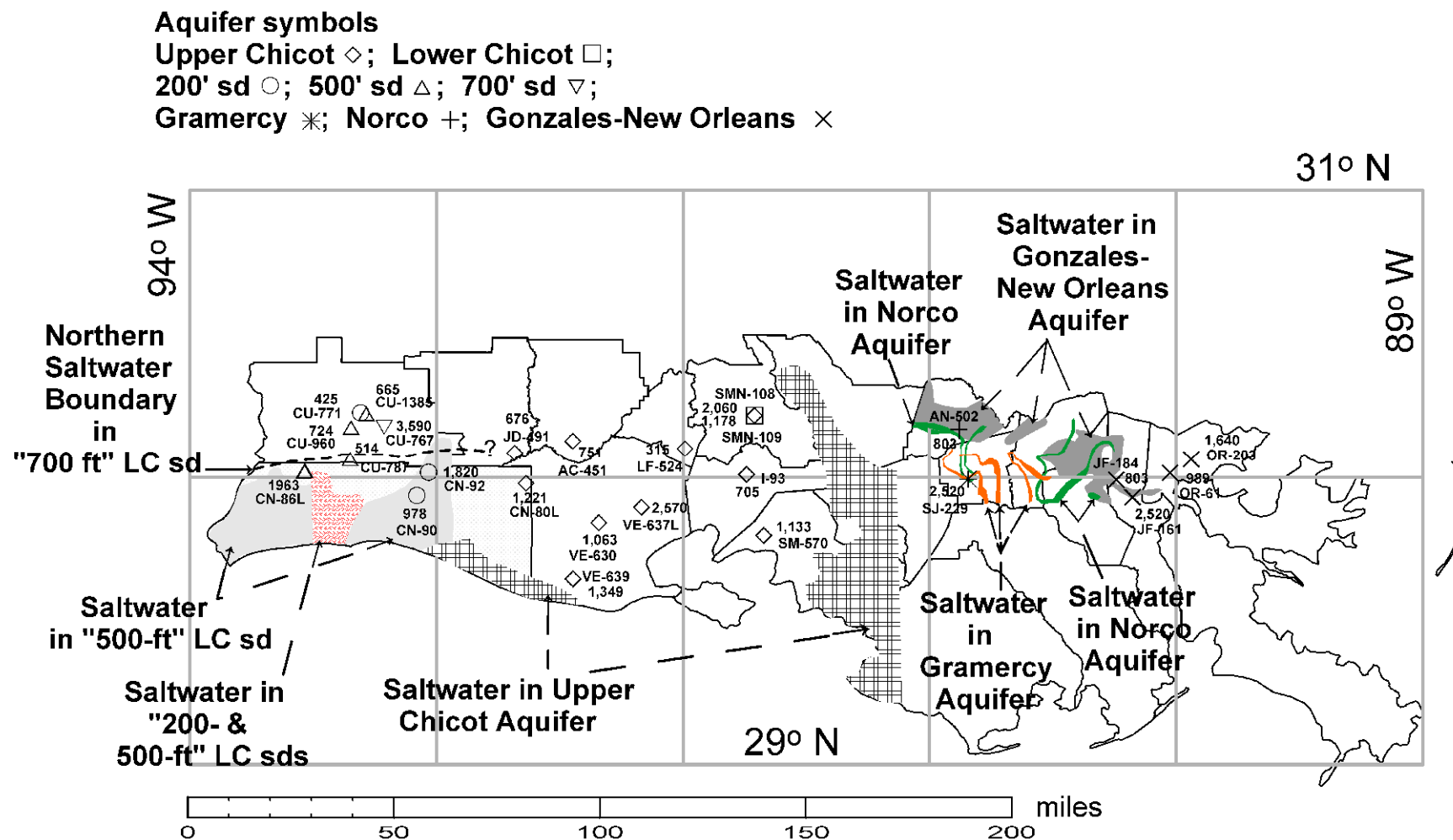
St. Tammany Parish

The St. Tammany area is similar to BRAS in that it lies just north of the South Louisiana region of salt diapirs (Ewing and Lopez, 1991). Nyman and Fayard (1978) documented brackish waters in the 1,500 ft (460 m) deep Pliocene Big Branch Aquifer in St. Tammany Parish. The Big Branch Aquifer is an artesian aquifer on the updip side of the BR-DS Fault on the north shore of Lake Pontchartrain (Figure 1). The Big Branch is contained within a sequence of fresh water aquifers, which are uncontaminated by

saltwater intrusion. The recharge into the Big Branch Aquifer has been suggested to occur by leakage across confining clays because the aquifer lacks surface recharge. Seismic data shows the aquifer may also lack a downdip section to the south under Lake Pontchartrain. Nyman and Fayard (1978) proposed the *in situ* brackish waters represented incomplete flushing in the area, presumably of fresh waters, which filled the pores of the aquifer in response to lowered sea level during the late Wisconsin Glaciation and have since been flushed by updip moving marine waters.

Coastal Parishes

The coastal parishes of Louisiana also overlie the South Louisiana region of salt diapirs. The shallow Pleistocene aquifers in coastal parishes are part of the regional Chicot Aquifer System. Areas of saltwater intrusion in the aquifer system shown in Figure 7 are from Nyman (1984) and Lovelace (1999) in southwest and south-central Louisiana, and from Tomaszewski (2003) in the New Orleans area of southeast Louisiana. The coastal parishes are cut by numerous east-west trending gravity faults and include numerous salt diapirs (Ewing and Lopez, 1991). Brackish waters occur in the 200, 500, and 700 ft Lake Charles sands in southwest Louisiana, the Upper and Lower Chicot sands in south-central Louisiana, and in the Gramercy, Norco, and the Gonzales-New Orleans Aquifers in southeast Louisiana. From west to east, the 200 and 700 ft sands grade into the Upper and Lower Chicot sands, respectively, and the 500 ft sand pinches out, just east of the Calcasieu Parish Boundary. Continuity of these Pleistocene sands with those in the New Orleans-Gonzales Aquifer System further east



C

Figure 7 Coastal Parishes sample locations used to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids (modified from Sotessell and Prochaska 2005).

is unknown. Nyman (1984) attributed the *in situ* brackish waters in the Chicot Aquifer System to a combination of updip movement of marine pore waters within an aquifer, vertical leakage from underlying aquifers containing saltwater, e.g., from the 700 ft Lake Charles sand into the 500 ft Lake Charles sand, and saltwater coning from the base of an aquifer. These processes are driven by the discharge of fresh water in wells at a rate faster than surface aquifer recharge of the fresh water. The saltwater front in the most heavily pumped aquifer in southwest Louisiana, the 500 ft sand, may be slowly moving northward from the border of Calcasieu and Cameron Parishes (Lovelace, 1999).

Methodology

Groundwater Sample Collection

Groundwater wells in the Baton Rouge Area (26) and Coastal Parishes (26) were sampled, respectively, in 2003 and in 2004 with the assistance of the US Geological Survey (Figures 7 and 8). The wells were largely owned and operated by the US Geological Survey to monitor the groundwater conditions in the area. Owners of the other wells sampled were in agreements with the US Geological Survey to allow access for study purposes. The St. Tammany Parish wells were sampled in 2001 through 2003 (Figure 9). Four of these wells (ST-RC1 to ST-RC4) were unregistered in the Louisiana Department of Transportation and Development system and completion depths were identified by Richard Chabreck, a St. Tammany water-well driller.

The locations of the monitor wells were chosen to include brackish and fresh groundwater samples and well accessibility. Because saltwater is denser than fresh water, saltwater encroaches into a fresh water aquifer as a wedge, and the leading edge moves along the base of the aquifer as a thin layer. Because large-diameter production wells typically have screens that are several tens of feet long, water withdrawn from the well is a mixture of water entering the screen at various depths along the screen. When chloride concentrations at such wells exceed 10 mg/L, it probably is an indication that a thin layer of saltwater with a higher chloride concentration is present at the base of the

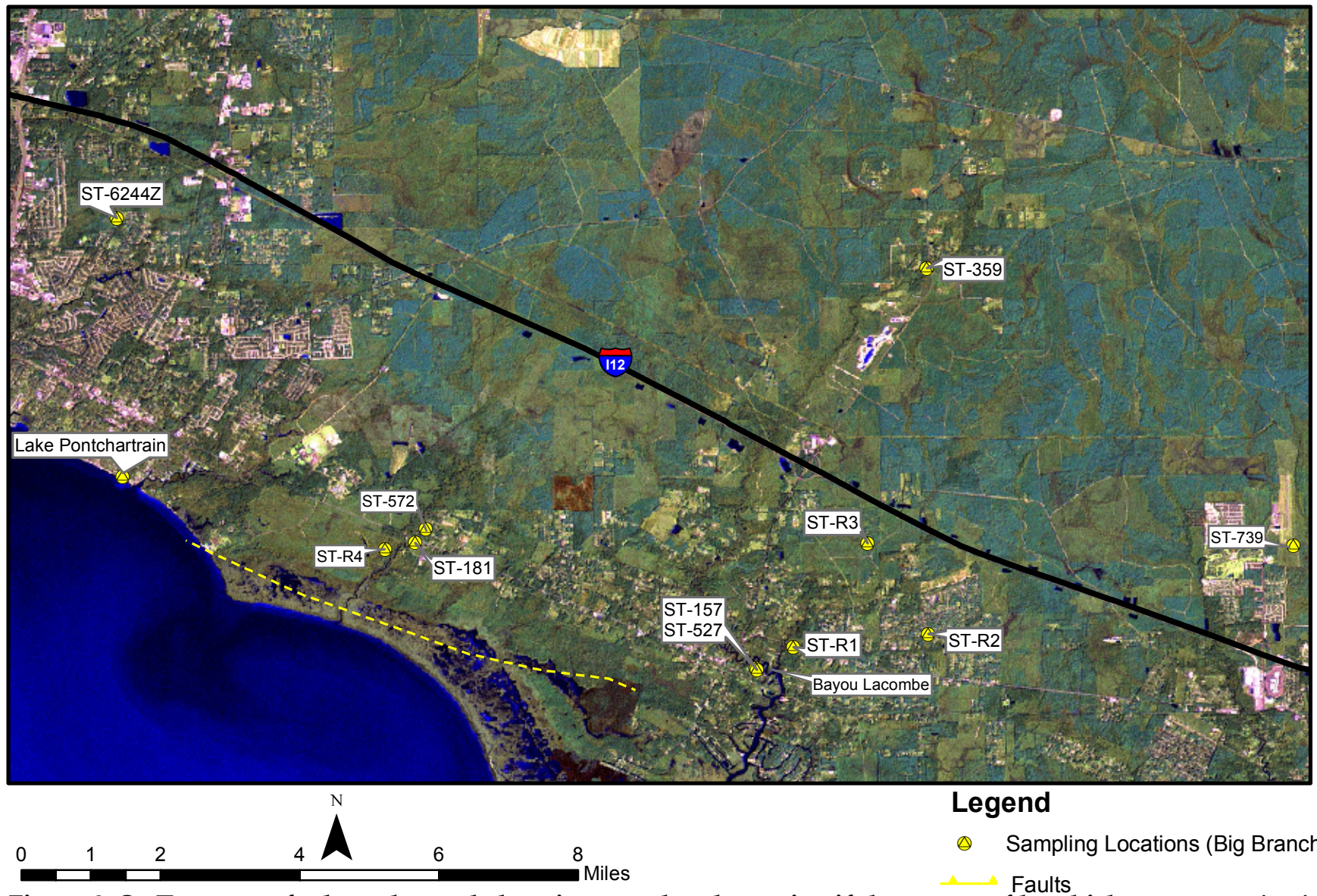


Figure 9: St. Tammany fault and sample locations used to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids (modified from Lopez, et. al, 1997).

aquifer, but is being mixed in the well with overlying fresh water that also is entering the screen.

The monitor wells were sampled using a permanently mounted turbine pump or by injection of compressed air through tubing below the water level to force the water to the surface. A minimum of two well volumes of water was purged prior to sampling except for the wells located in the St. Tammany area (Figure 10). The St. Tammany wells were artesian; therefore, no pump mechanism or prior purging volume was necessary. When available, a Hydrolab Quanta G probe was used to measure *in situ* field parameters for specific conductivity, Eh, temperature, dissolved oxygen, and pH. Only specific conductivity measurements were reported for field parameters of samples collected by injection of compressed air due to the potential of the sampling methodology affecting the other field parameters.



Figure 10 Example monitoring well sampled using compressed air.

Upon the completion of purging activities, the groundwater samples were collected and placed into 250 ml acid-washed sample containers. The sample containers were immediately placed on ice to maintain a temperature of approximately 4°C during storage and transport to the University of New Orleans (UNO). The samples were gravity-filtered through #42 micron Whitman filter and subsequently measured for alkalinity within eight hours of sample collection. Alkalinity was measured in accordance with ASTM D1067 – 06: Standard Test Methods for Acidity or Alkalinity of Water using a pH titration to a pH of 4.5 with 0.01 molar HCl on a filtered sample. The remaining filtered sample was split into two 60 ml aliquots with one of the aliquots acidified with reagent-grade HCl for cation analyses. All samples were refrigerated at UNO until analyzed.

Groundwater Analysis

Groundwater samples were analyzed for cations, anions, and aqueous silicon and strontium isotopes. Sample analysis was performed at the UNO geology wet chemistry laboratory except for strontium isotopes. Twenty brackish water samples were submitted to Louisiana State University Geochemical Laboratories for analysis.

Measurements of aqueous component concentrations were completed within six weeks of collection at the UNO geochemistry laboratory using Dionix 100 and Dionix 1000 ion chromatographs (IC) for cations (acidified aliquot) and anions (non-acidified aliquot). Aqueous silicon concentrations were measured colorimetrically by the molybdenum blue method on a Turner 690 UV-VIS spectrograph. Isotopic ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ samples were measured at Louisiana State University Isotope Laboratory of Dr. Lui Chan on filtered samples using a Finnigan MAT 262 mass spectrometer within nine months of collection. Analytical precisions were 1 mg l⁻¹ HCO₃ for alkalinities, 0.05 mg l⁻¹ for cations, other anions, and aqueous SiO₂, and 0.00001 for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. A summary of the analytical results are reported Tables 2 through 5. The data from outside the Baton Rouge area are from groundwater compositions listed in Table 3 of Stoessell and Prochaska, (2005).

Table 2 Baton Rouge Aquifer System groundwater data collected to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids.

Well ID	Aquifer	Lat	Long	Well Depth (ft)	Date Sample Collected	Specific Conductivity (μs/cm)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Sr (mM)	SiO ₂ (mM)	Br (mM)	Cl (mM)	SO ₄ (mM)	Alkalinity as HCO ₃ (mM)	Electrical Balance (meq/l)	tds (mg/l)	⁸⁷ Sr/ ⁸⁶ Sr
EB-1017C	400' Sand	30.402	91.037	567	12/2003	308	3.132	0.009	0.004	0.012	b.a.p.	0.572	b.a.p.	0.104	0.078	2.983	-0.07	300	n.m.
EB-1028	2,000' Sand	30.435	91.169	2,238	11/2003	1,156	10.147	0.027	0.021	0.143	0.001	0.606	0.003	6.865	0.067	3.327	0.17	730	0.708
EB-1149	2,400' Sand	30.448	91.177	2,694	11/2003	386	4.073	0.015	0.001	0.035	b.a.p.	0.373	b.a.p.	0.078	0.112	3.901	-0.04	370	n.m.
EB-1150	2,000' Sand	30.448	91.177	2,242	11/2003	833	7.717	0.024	0.013	0.147	0.001	0.408	0.002	4.178	0.096	3.704	-0.01	593	n.m.
EB-1253	2,300' Sand	30.448	91.190	2,687	11/2003	408	4.428	0.018	0.002	0.028	b.a.p.	0.398	b.a.p.	0.089	0.113	4.245	-0.05	401	n.m.
EB-413	1,500' Sand	30.445	91.142	1,745	11/2003	327	3.597	0.010	0.003	0.013	b.a.p.	0.479	b.a.p.	0.271	0.105	3.212	-0.06	328	n.m.
EB-434	600' Sand	30.439	91.178	611	11/2003	441	3.855	0.039	0.046	0.153	0.001	0.581	0.001	1.354	0.043	2.802	0.05	356	n.m.
EB-621	1,200' Sand	30.417	91.090	1,487	12/2003	545	5.175	0.013	0.008	0.105	0.001	0.479	0.001	1.732	0.109	3.327	0.14	428	n.m.
EB-630	2,000' Sand	30.448	91.190	2,253	11/2003	643	6.485	0.019	0.005	0.053	b.a.p.	0.404	0.001	2.490	0.089	3.868	0.08	509	n.m.
EB-750	2,800' Sand	30.528	91.197	2,643	11/2003	728	7.521	0.024	0.003	0.033	b.a.p.	0.418	0.001	1.865	0.045	5.589	0.07	612	n.m.
EB-771	1,500' Sand	30.446	91.144	1,739	11/2003	315	3.574	0.011	0.004	0.022	b.a.p.	0.524	b.a.p.	0.120	0.099	3.179	0.14	323	n.m.
EB-778	2,000' Sand	30.419	91.141	2,586	12/2003	1,012	9.810	0.026	0.006	0.035	b.a.p.	0.393	0.002	4.202	0.028	5.408	0.25	734	0.708
EB-780A	1,200' Sand	30.419	91.141	1,622	11/2003	3,260	27.100	0.076	0.170	1.013	0.018	0.111	0.013	26.710	0.000	1.999	0.86	1,749	0.708
EB-782A	1,000' Sand	30.427	91.151	1,189	01/2003	1,800	16.220	0.041	0.048	0.255	0.003	0.323	0.007	12.830	0.016	3.507	0.50	1,076	0.708
EB-783B	2,000' Sand	30.417	91.193	2,675	12/2003	3,340	32.540	0.072	0.016	0.046	0.001	0.348	0.011	20.790	0.000	10.522	1.42	2,154	0.708
EB-792B	2,000' Sand	30.435	91.135	2,286	11/2003	387	3.978	0.013	0.002	0.025	b.a.p.	0.411	b.a.p.	0.077	0.104	3.819	-0.06	363	n.m.
EB-798	2,800' Sand	30.526	91.175	2,647	11/2003	1,660	14.620	0.052	0.021	0.189	0.003	0.362	0.004	8.740	0.022	5.408	0.90	1,011	0.708

Table 2(continued) Baton Rouge Aquifer System groundwater data collected to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids.

Well ID	Aquifer	Lat	Long	Well Depth (ft)	Date Sample Collected	Specific Conductivity (μs/cm)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Sr (mM)	SiO ₂ (mM)	Br (mM)	Cl (mM)	SO ₄ (mM)	Alkalinity as HCO ₃ (mM)	Electrical Balance (meq/l)	tds (mg/l)	⁸⁷ Sr/ ⁸⁶ Sr
EB-803B	2,000' Sand	30.385	91.041	2,565	12/2003	2,270	21.450	0.067	0.082	0.239	0.005	0.343	0.007	16.610	0.006	4.704	0.84	1,405	0.709
EB-804A	1,700' Sand	30.408	91.064	1,950	01/2003	375	4.004	0.012	0.002	0.016	b.a.p.	0.399	b.a.p.	0.055	0.109	3.540	0.24	346	n.m.
EB-804B	2,400' Sand	30.408	91.064	2,762	11/2003	782	7.310	0.023	0.003	0.072	b.a.p.	0.393	0.002	3.376	0.089	3.507	0.42	538	n.m.
EB-805	1,000' Sand	30.408	91.064	1,072	11/2003	24,900	195.202	0.270	9.714	18.450	0.106	0.366	0.111	251.181	b.a.p.	2.229	-1.51	14,555	0.708
EB-825	400' Sand	30.431	91.156	475	11/2003	275	2.786	0.027	0.042	0.075	0.001	0.800	b.a.p.	0.107	0.072	2.655	0.14	290	n.m.
EB-870	600' Sand	30.458	91.168	692	11/2003	288	2.661	0.033	0.034	0.107	0.001	0.672	b.a.p.	0.081	0.102	2.737	-0.05	288	n.m.
EB-917	1,500' Sand	30.437	91.142	1,736	11/2003	439	4.208	0.014	0.003	0.016	b.a.p.	0.409	0.001	1.222	0.100	2.884	-0.05	352	n.m.
EB-918	1,500' Sand	30.430	91.129	1,834	12/2003	2,740	23.450	0.059	0.172	1.103	0.005	0.370	0.011	21.940	0.063	2.327	1.67	1,539	0.708
EB-990	1,200' Sand	30.419	91.065	1,450	12/2003	317	3.152	0.009	0.003	0.033	b.a.p.	0.456	b.a.p.	0.069	0.116	2.999	-0.07	298	n.m.
WB-112	1,500' Sand	30.431	91.211	2,205	12/2003	627	5.988	0.022	0.008	0.045	b.a.p.	0.817	0.001	2.230	0.083	3.786	-0.07	508	n.m.
WB-113	1,500' Sand	30.430	91.209	2,242	12/2003	1,135	10.726	0.028	0.013	0.135	0.001	0.656	0.003	6.129	0.057	4.900	-0.10	815	0.708
WB-136	1,200' Sand	30.453	91.249	1,305	12/2003	279	2.955	0.010	0.004	0.010	b.a.p.	0.639	b.a.p.	0.096	0.098	2.721	-0.02	286	n.m.
WB-151	2,400' Sand	30.445	91.149	2,658	11/2003	335	3.680	0.013	0.002	0.030	b.a.p.	0.411	b.a.p.	0.073	0.108	3.327	0.14	327	n.m.
WB-173	1,500' Sand	30.416	91.217	2,194	12/2003	412	4.075	0.011	0.003	0.020	b.a.p.	0.463	b.a.p.	0.828	0.091	3.163	-0.04	354	n.m.
WB-181	1,700' Sand	30.446	91.203	1,900	12/2003	292	3.081	0.010	0.001	0.012	b.a.p.	0.398	b.a.p.	0.082	0.091	2.852	0.00	281	n.m.
WB-35	1,200' Sand	30.449	91.212	1,290	12/2003	305	3.225	0.010	0.004	0.011	b.a.p.	0.473	b.a.p.	0.079	0.111	3.048	-0.08	303	n.m.

Notes: μs/cm = micro Siemens, mM = millimolar, b.a.p. = below analytical precision

Table 3 Coastal Parishes Aquifer System groundwater data collected to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids (from Stoessell and Prochaska, 2005).

Well ID	Aquifer	Lat	Long	Well Depth (ft)	Date Sample Collected	Specific Conductivity (μs/cm)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Sr (mM)	SiO ₂ (mM)	Br (mM)	Cl (mM)	SO ₄ (mM)	Alkalinity as HCO ₃ (mM)	Electrical Balance (meq/l)	tds (mg/l)	⁸⁷ Sr/ ⁸⁶ Sr
SM-57U	Upper Chicot	29.797	91.673	638	03/2004	1133	5.437	0.069	1.234	1.921	0.004	0.575	0.003	5.387	0.001	6.162	0.27	837	n.m.
SMN-109	Upper Chicot	30.218	91.711	375	3/2004	1178	6.960	0.069	1.139	1.944	0.012	0.619	0.002	3.526	b.a.p.	9.130	0.56	989	n.m.
SMN-108	Lower Chicot	30.218	91.711	505	3/2004	2060	15.529	0.092	1.226	2.056	0.013	0.549	0.006	11.536	b.a.p.	9.424	1.24	1491	0.7
I-93	Upper Chicot	30.010	91.743	585	3/2004	705	2.927	0.044	0.888	1.629	0.005	0.653	b.a.p.	1.120	b.a.p.	6.670	0.23	642	n.m.
LF-524	Upper Chicot	30.101	91.993	174	3/2004	315	2.449	0.095	0.211	0.352	0.001	0.758	b.a.p.	0.217	0.024	3.376	0.03	341	n.m.
VE-630	Upper Chicot	29.842	92.342	498	3/2004	1063	6.177	0.062	1.168	1.657	0.006	0.525	0.003	5.218	b.a.p.	7.195	-0.52	896	n.m.
VE-637L	Upper Chicot	29.896	92.169	243	3/2004	2570	15.137	0.078	1.814	4.092	0.006	0.569	0.009	21.973	b.a.p.	6.179	-1.12	1751	0.7
VE-639	Upper Chicot	29.646	92.447	608	3/2004	1349	9.004	0.072	1.045	1.704	0.011	0.456	0.005	8.885	b.a.p.	6.375	-0.67	1036	n.m.
AC-451	Upper Chicot	30.128	92.447	293	3/2004	751	4.915	0.068	0.551	1.140	0.007	0.514	0.001	1.125	0.001	7.408	-0.16	698	n.m.
JD-491	Upper Chicot	30.086	92.682	377	3/2004	676	3.802	0.043	0.477	1.050	0.003	0.680	0.002	2.849	b.a.p.	4.196	-0.14	541	n.m.
CN-80L	Upper Chicot	29.979	92.636	481	3/2004	1221	7.612	0.067	0.810	1.452	0.009	0.425	0.004	7.785	b.a.p.	4.949	-0.52	860	n.m.
CN-92	200-ft Sand	30.018	93.032	443	3/2004	1820	13.006	0.065	0.621	1.275	0.008	0.467	0.006	11.621	0.016	5.490	-0.27	1146	0.7
CN-90	200-ft Sand	29.936	93.080	396	3/2004	978	7.656	0.042	0.342	0.609	0.003	0.438	0.003	4.851	b.a.p.	4.687	0.06	695	n.m.
CN-88L	500-ft Sand	30.015	93.158	804	3/2004	2360	18.791	0.073	0.402	0.936	0.008	0.468	0.009	16.303	0.002	5.031	0.21	1397	n.m.
CN-86L	500-ft Sand	30.022	93.536	641	3/2004	1963	16.790	0.048	0.229	0.556	0.004	0.478	0.007	14.442	b.a.p.	4.736	-0.77	1246	0.7

Table 3 (continued) Coastal Parishes Aquifer System groundwater data collected to determine if the source of brackish waters are in situ down dip marine pore waters or from deeper marine formation fluids (from Stoessell and Prochaska, 2005).

Well ID	Aquifer	Lat	Long	Well Depth (ft)	Date Sample Collected	Specific Conductivity (μs/cm)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Sr (mM)	SiO ₂ (mM)	Br (mM)	Cl (mM)	SO ₄ (mM)	Alkalinity as HCO ₃ (mM)	Electrical Balance (meq/l)	tds (mg/l)	⁸⁷ Sr/ ⁸⁶ Sr
CU-771	200-ft Sand	30.227	93.308	241	3/2004	425	2.423	0.045	0.332	0.676	0.004	0.394	0.000	0.494	0.020	4.081	-0.12	385	n.m.
CU-960	500-ft Sand	30.175	93.347	598	3/2004	724	3.040	0.085	0.588	1.260	0.009	0.909	0.002	3.780	0.001	3.016	0.04	512	n.m.
CU-787	500-ft Sand	30.065	93.351	734	3/2004	514	3.362	0.043	0.232	0.686	0.003	0.565	0.001	1.314	0.001	3.999	-0.07	437	n.m.
CU-1385	500-ft Sand	30.223	93.285	580	3/2004	665	4.363	0.062	0.351	0.998	0.003	0.836	0.002	3.018	0.004	3.360	0.74	514	n.m.
CU-767	700-ft Sand	30.177	93.212	850	3/2004	3590	24.837	0.141	1.394	2.994	0.014	0.704	0.015	29.899	0.000	4.294	-0.43	2097	0.7
AN-502	Norco-Gonzales	30.166	90.881	300	09/2004	803	5.437	0.047	0.389	0.654	0.003	0.446	0.003	4.090	0.002	3.786	-0.31	566	0.7
JF-161	Norco-Gonzales	29.930	90.178	772	10/2004	2520	23.271	0.116	0.302	0.465	0.004	0.468	0.010	17.262	0.002	6.441	1.21	1600	n.m.
JF-184	Norco-Gonzales	29.991	90.243	704	09/2004	803	7.482	0.046	0.066	0.104	b.a.p.	0.481	0.003	3.892	0.002	4.179	-0.21	602	n.m.
OR-61	Norco-Gonzales	30.016	90.026	653	09/2004	989	9.830	0.102	0.091	0.125	0.001	0.429	0.003	2.713	0.012	7.752	-0.13	834	n.m.
OR-203	Norco-Gonzales	30.064	89.940	453	09/2004	1640	14.920	0.102	0.183	0.091	b.a.p.	0.367	0.006	10.041	0.001	6.015	-0.50	1101	n.m.
SJ-229	Gramercy	29.994	90.845	345	09/2004	1253	6.116	0.086	1.308	2.161	0.010	0.549	0.004	5.585	0.001	8.637	-1.07	1022	0.7

Notes: μs/cm = micro Siemens, mM = millimolar, meq/l = milliequivalent per liter, mg/l = milligrams per liter, n.m. = not measured, b.a.p. = below analytical precision

Table 4 St. Tammany Aquifer System Groundwater data collected to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids (from Stoessell and Prochaska, 2005) .

Well ID	Aquifer	Lat	Long	Well Depth (ft)	Date Sample Collected	Specific Conductivity (μs/cm)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Sr (mM)	SiO ₂ (mM)	Br (mM)	Cl (mM)	SO ₄ (mM)	Alkalinity as HCO ₃ (mM)	Electrical Balance (meq/l)	tds (mg/l)	⁸⁷ Sr/ ⁸⁶ Sr
ST-157	Big Branch	30.310	89.931	1503	09/2001	5830	47.9	0.07	0.42	0.699	0	0.33	0.023	47.39	0	5.2444	-2.4325	3165	0.7
ST-181	Big Branch	30.336	90.002	1509	02/2002	553	5.31	0.01	b.a.p.	0.018	b.a.p.	0.45	9E-04	1.64	0.108	3.2778	0.2217	418.9	n.m.
ST-359	Big Branch	30.393	89.896	1253	11/2001	552	6.05	0.01	0	0.022	b.a.p.	0.31	b.a.p.	0.08	0.123	5.5722	0.2072	513.7	n.m.
ST-572	Big Branch	30.339	90.000	1501	11/2001	539	5.05	0.01	0	0.015	b.a.p.	0.37	0.001	1.59	0.107	3.2122	0.0804	402.1	n.m.
ST-739	Big Branch	30.342	89.823	1576	11/2001	388	4.78	0.01	0	0.013	b.a.p.	0.46	b.a.p.	0.07	0.126	4.2119	0.2821	410	n.m.
ST-6244Z	Big Branch	30.404	90.064	1460	11/2001	278	3.06	0	0	0.042	b.a.p.	0.52	b.a.p.	0.08	0.096	2.7533	0.1271	283.5	n.m.
ST-R1	Big Branch	30.314	89.924	n.m.	07/2003	3690	33.62	0.06	0.25	0.432	0	0.32	0.015	29.9	0.017	4.9986	0.1088	2186	0.7
ST-R2	Big Branch	30.322	89.903	1500	10/2001	3350	29.1	0.04	0.14	0.294	0	0.32	0.012	27.84	0.002	4.8675	-2.7071	1990	0.7
ST-R3	Big Branch	30.332	89.991	n.m.	11/2001	659	6.26	0.01	0.01	0.027	b.a.p.	0.38	0.001	2.85	0.088	3.3761	-0.0685	484.3	n.m.
ST-R4	Big Branch	30.339	90.014	n.m.	10/2001	641	5.83	0.01	0.01	0.027	b.a.p.	0.37	0.001	2.34	0.101	3.4417	-0.0808	460.9	n.m.

Notes: μs/cm = micro Siemens, mM = millimolar, meq/l = milliequivalent per liter, mg/l = milligrams per liter, n.m. = not measured, b.a.p. = below analytical precision

Table 5 Surface water data used to determine if the source of brackish waters are *in situ* down dip marine pore waters or from deeper marine formation fluids (from Stoessell and Prochaska, 2005).

Sample ID	Depth (ft)	Date Sample Collected	Specific Conductivity (μs/cm)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Sr (mM)	SiO ₂ (mM)	Br (mM)	Cl (mM)	SO ₄ (mM)	Alkalinity as HCO ₃ (mM)	Electrical Balance (meq/l)	tds (mg/l)	⁸⁷ Sr/ ⁸⁶ Sr
Lake Pontchartrain	1	10/2001	4,030	27.60	0.563	2.715	0.699	0.004	0.115	0.046	30.74	1.447	0.623	0.695	2,028	n.m.
Bayou Lacombe	1	10/2001	540	2.910	0.043	0.197	0.107	0.001	0.186	0.004	3.050	0.125	0.213	0.046	222	n.m.

Notes: μs/cm = micro Siemens, mM = millimolar, meq/l = milliequivalent per liter, mg/l = milligrams per liter, n.m. = not measured

Data Assessment

Recharging of the aquifers is assumed to be from a mixture of surface water sources that includes fresh and brackish water. To chemically fingerprint the saltwater source, the following relationships of Br, Cl, Na, K, Sr^{87} , and Sr^{86} were assessed. These components are commonly used to chemically fingerprint saltwater sources (e.g. Carpenter (1978), Land and Prezbindowski (1981), Stoessell and Moore (1983), and Stoessell (1997).

Linear mixing trends were determined by plotting the concentrations of one conserved component versus a second conserved component, e.g., Br versus Cl, and by plotting the concentration ratio of the two conserved components versus the reciprocal of the concentration of the component in the denominator, e.g., Br/Cl versus Cl^{-1} . The first plot focuses on the more saline samples, and the second plot expands the dilute region to show how well the dilute samples fit a linear mixing relationship. The intercept on the second plot accurately delineates the slope of a trend line on the first plot, useful because of scatter in the mixing line. The intercept is usually close to the value of the ratio in the saltwater end member because its salt composition dominates the mixture.

Aqueous $\text{Sr}^{87}/\text{Sr}^{86}$ ratios can help set minimum age limits for marine Cenozoic formation fluids, which have acted as saltwater end members. Since Late Eocene, the isotopic ratio has steadily increased in seawater due to decay of Rubidium 87 (Rb^{87}) to Sr^{87} and its subsequent input into the oceans through weathering reactions (Faure, 1998), making this a convenient fluid dating tool. However, if the marine formation fluid subsequently moves upward through other formations, the isotopic ratio may be elevated by mixing with a younger marine fluid and/or by picking up additional Sr^{87} generated from Rb^{87} decay in clays and feldspar, producing an apparent younger age. If Sr is conserved, plotting the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios against the reciprocal of the total Sr concentrations produces a linear mixing line in which the intercept is an estimate of the Sr isotope ratio in the saltwater end member. Generally, the mixing line is expected to

have a positive slope because younger pore waters are expected to have higher isotope ratios.

Results and Discussion

Groundwater Sample Results

Laboratory analysis detected concentrations of common saltwater components of Br, Cl, Na, K and Sr in groundwater and surface water samples collected during this study. Tables 2 through 5 provide summary of the detected elements. Where available, field measurements for specific conductivity are also reported. It was noted during collection of some of the samples a strong H₂S odor was observed. A number of elements in some samples did not meet analytical precision requirements; therefore, they were not analyzed as part of the dataset.

Mixing Trends

Mixing trends were plotted in Millimolarity (mM) units. The linear mixing trends are shown in the A and B plots in Figures 11, 12, and 13, respectively, for Br, Na, and K. In each figure, the mM of a component is plotted versus mMCl in the A plot, and the mM ratio of the component to Cl is plotted versus (mMCl)⁻¹ in the B plot. The dashed seawater-mixing line in the figures was computed using the fresh water sample in Table 5 from Bayou Lacombe in St. Tammany (that flows into Lake Pontchartrain, an estuary of the Gulf of Mexico) and seawater (from Pytkowicz, 1985). The seawater ratio and the average South Louisiana Miocene formation fluid ratio (Collins, 1970) are also plotted on the B plot in each figure to indicate, respectively, the expected ratio for a Quaternary marine formation fluid and for a Neogene marine formation fluid that dissolved halite (Stoessell and Moore, 1983).

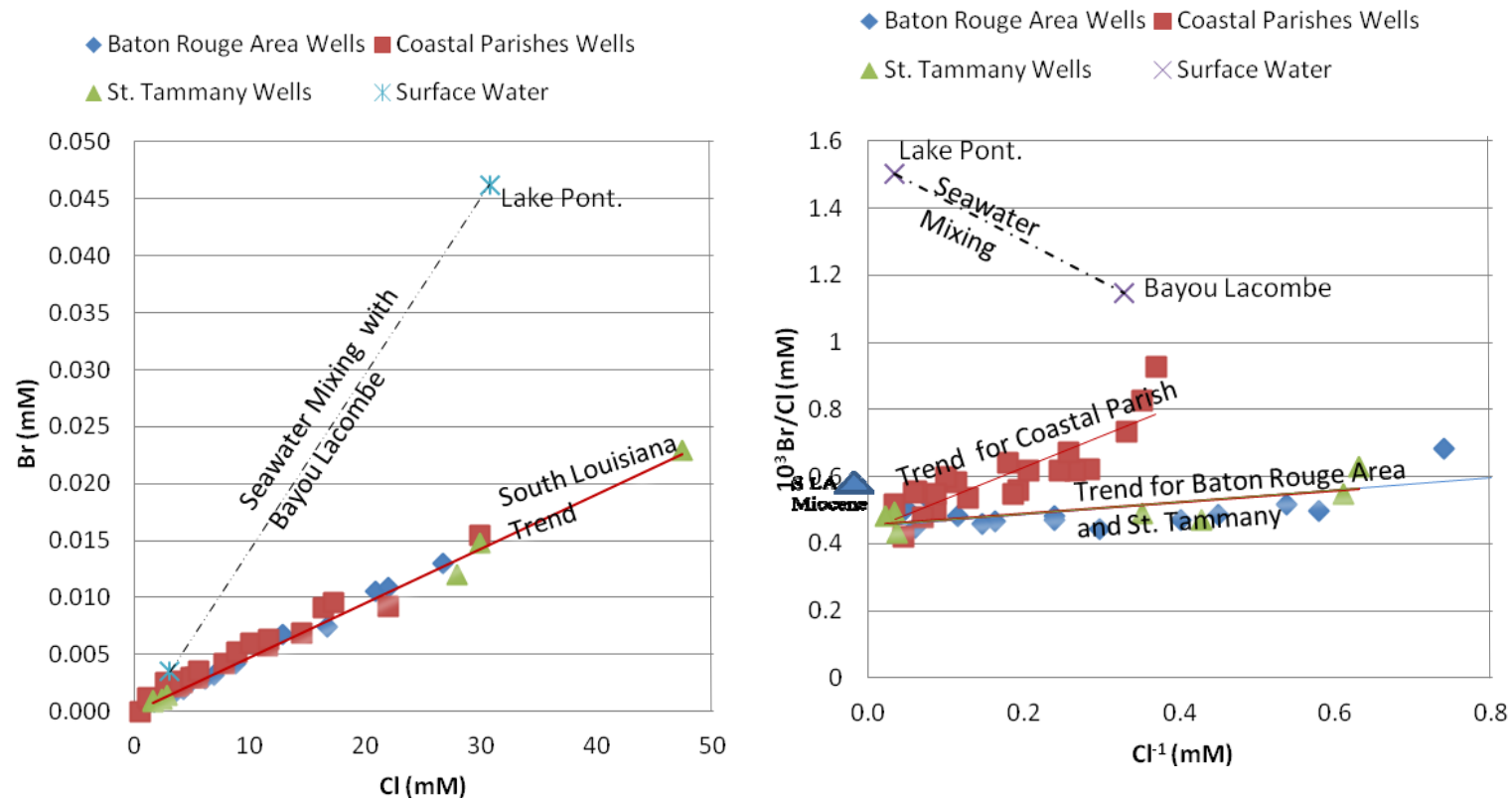


Figure 11 (A) Br versus Cl and (B) 10^3 Br/Cl versus $(\text{Cl})^{-1}$. The common intercept in Figure 11B the molar Br/Cl ratio in the saltwater source. This ratio is about 0.0005, below the average of South Louisiana Miocene formation fluid. This ratio "fingerprints" the saltwater source(s) as having increased salinity due to halite dissolution.

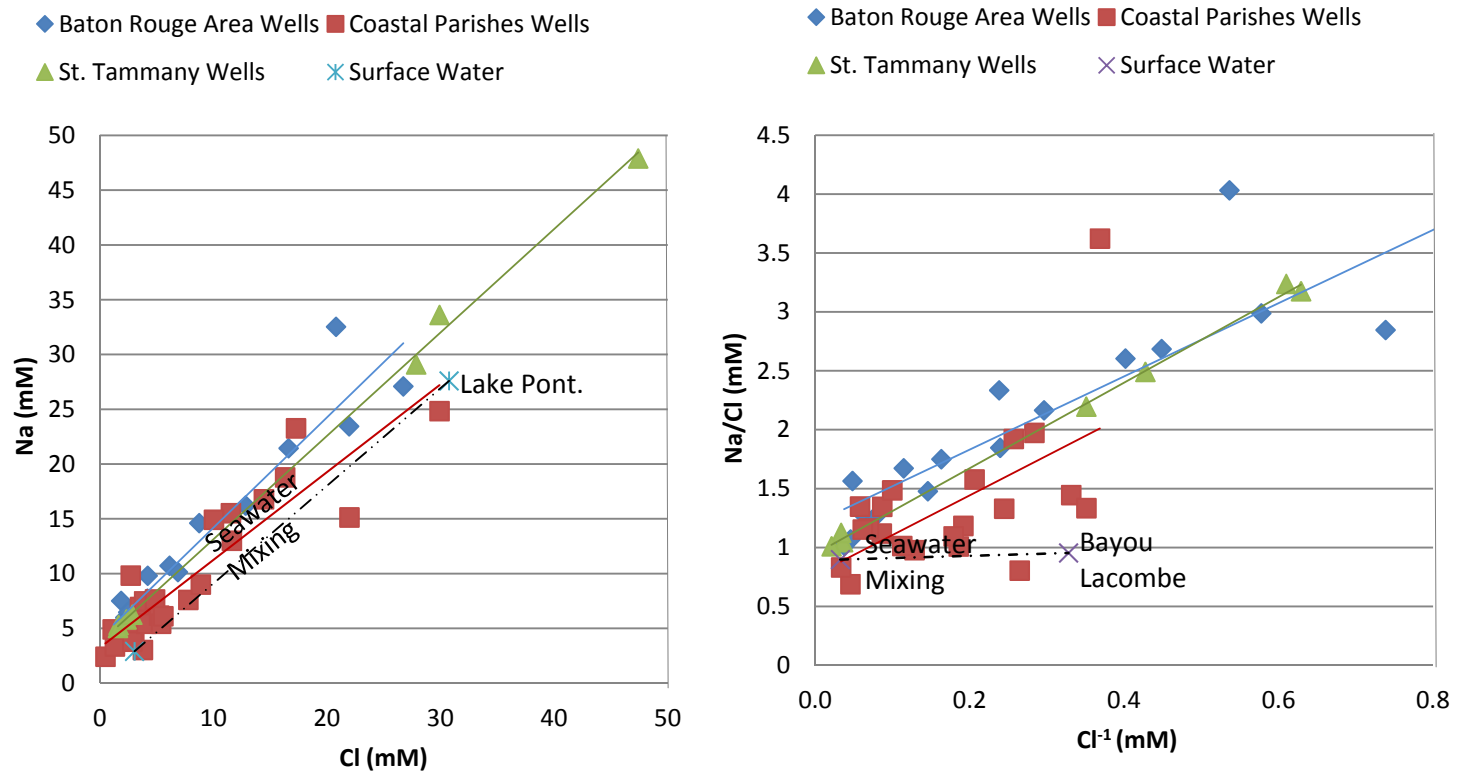


Figure 12 (A) Na versus Cl and (B) Na/Cl versus $(\text{Cl})^{-1}$ Halite dissolution will produce a molar Na/Cl ratio approaching one. All but four plot above the seawater-mixing line supporting halite dissolution as the salinity source.

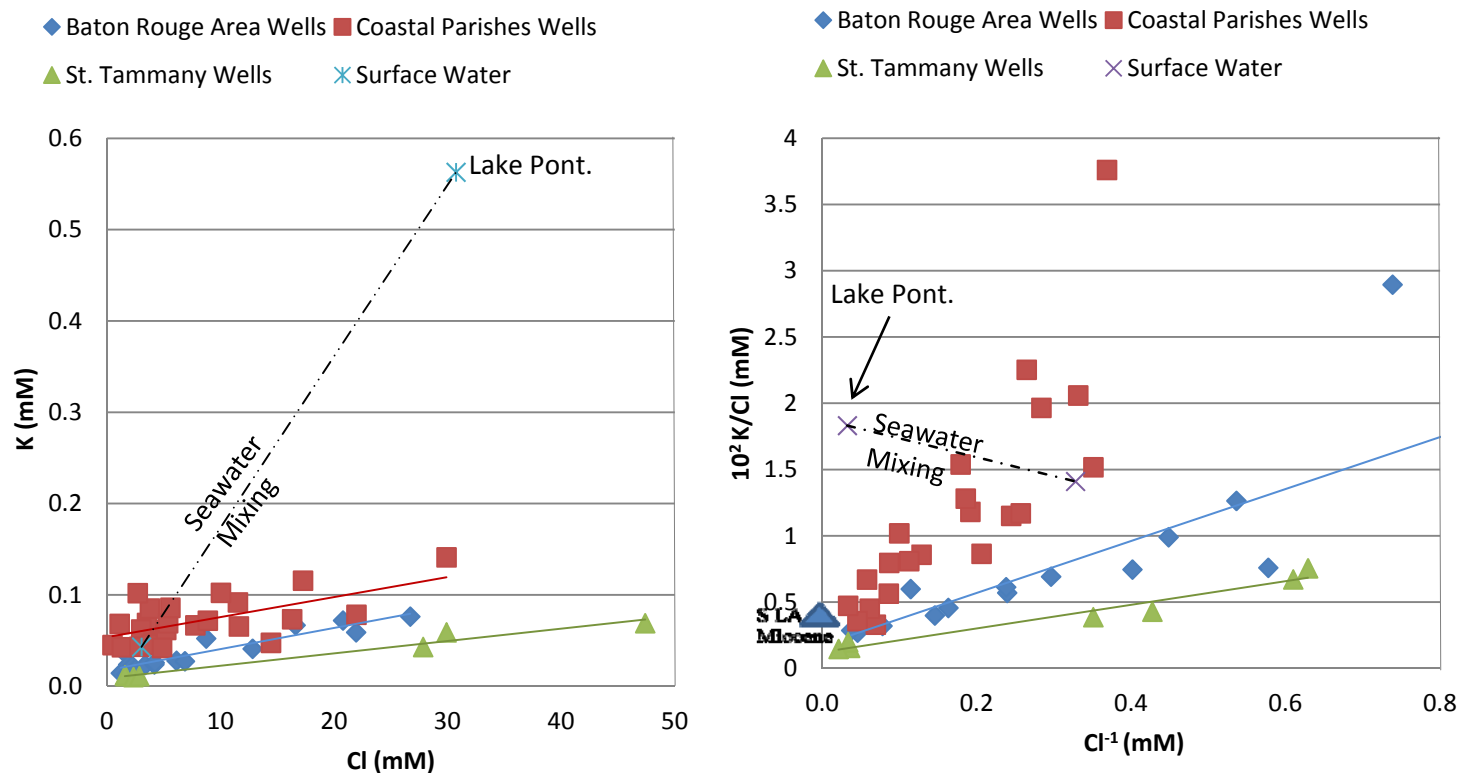


Figure 13 (A) K versus Cl and (B) $10^2 K/Cl$ versus $(Cl)^{-1}$ Figure 13B illustrates that the molar K/Cl ratios of samples converge towards a common intercept ranging from 0.0015 to 0.003, bracketing the ratio of 0.0029 for the average South Louisiana Miocene formation fluids (Collins, 1970). These ratios for the saltwater sources are more than a factor of six lower than in seawater.

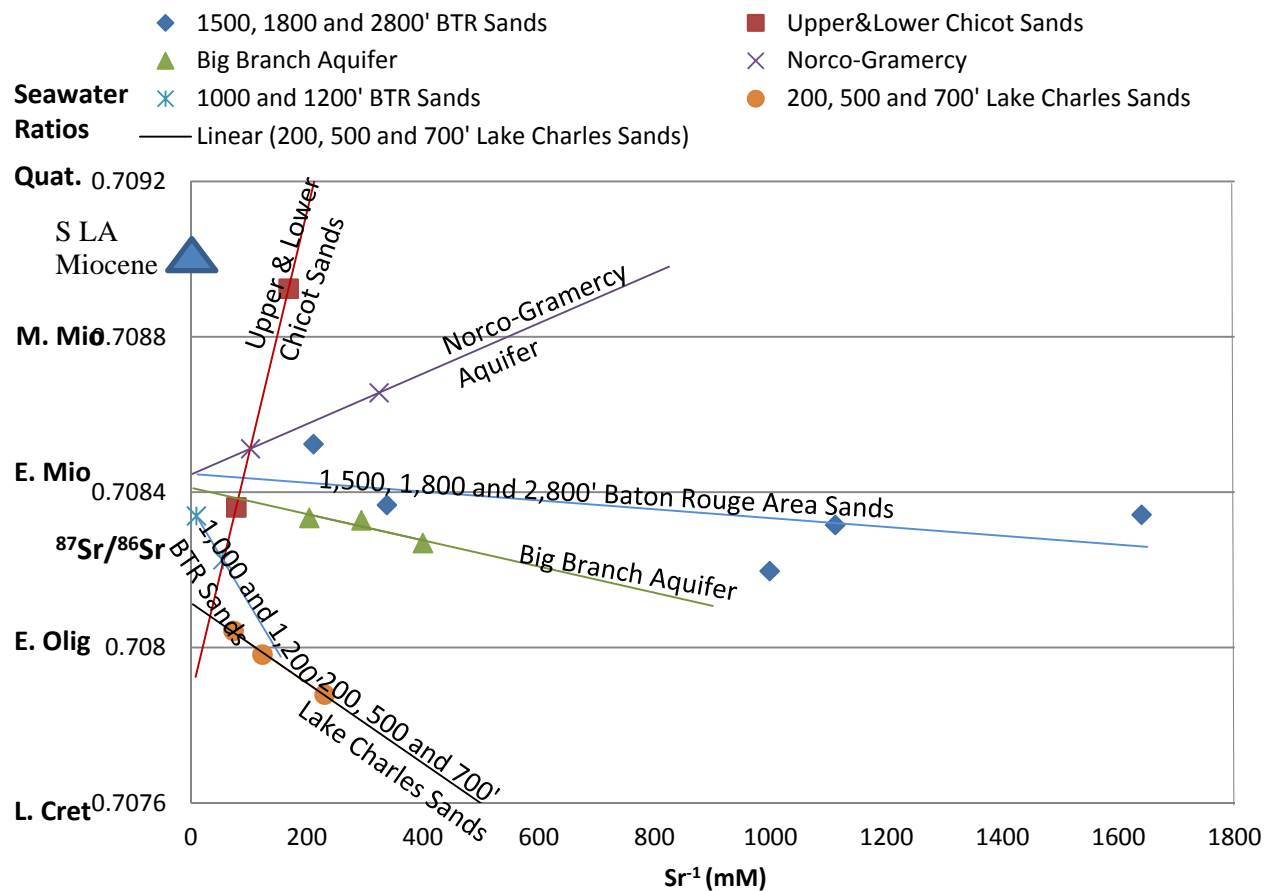


Figure 14 $^{87}\text{Sr}/^{86}\text{Sr}$ versus $(\text{Sr})^{-1}$ The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios are grouped by aquifer or group of adjacent aquifers and six mixing trends are shown in the figure. These ratios range from 0.7080 to 0.7085, corresponding to seawater ages of Middle Oligocene to Early Miocene, consistent with the saltwater sources being older formation fluids than in situ marine fluids in the Late Miocene to Pleistocene-age aquifers.

Bromide and Chloride

The linear mixing trend in Figure 11A for mM of Br versus Cl fits the samples from all the aquifers. Two trends occur in Figure 11B in which the molar ratio of Br/Cl is plotted versus the reciprocal of Cl concentration. The trends indicate the dilute waters in the coastal Pleistocene aquifers are enriched (reasons unknown at this time) in Br relative to those in the Baton Rouge and St. Tammany sands. The common intercept in Figure 11B for both trends gives the molar Br/Cl ratio in the saltwater source. This ratio is about 0.0005, close to the ratio in the average South Louisiana Miocene formation fluid (Collins, 1970) and a factor of 3 less than the ratio in seawater. This ratio “fingerprints” the saltwater source(s) as having increased salinity due to halite dissolution. The ratio can be explained by a marine formation fluid dissolving more than 70 grams of diagenetically recrystallized halite per liter of seawater (Stoessell and Prochaska, 2005), with the recrystallized halite containing an average of 50 mg Br/kg (Stoessell and Carpenter, 1986).

Sodium and Chloride

Halite dissolution will produce a molar Na/Cl ratio approaching one in the saltwater source, larger than the 0.86 ratio in seawater. The dissolution of 70 grams of halite dissolution per liter of marine pore fluids (mentioned above) would produce an aqueous molar Na/Cl ratio of 0.94. With the exceptions of 4 samples mentioned below, Na concentrations and molar Na/Cl ratios, respectively, plot above the seawater-mixing line in Figures 12A and 12B, supporting halite dissolution as the salinity source.

The scatter in the data in Figures 12A and 12B is likely due to water-rock interactions. In fresh waters at near-surface temperatures, Na is input from weathering feldspars and exchanged with calcium on clays (Berner, 1971). Na is commonly removed by albitization of Ca feldspar during diagenesis in deeper formations (Land and Prezbindowski, 1981). Three of the four exceptions (EB-805, VE-637L, and CU-767) are saline with high molar Ca/Na ratios, consistent with Na removal by albitization of

Ca feldspar, and the fourth sample (CU-960) is predominantly fresh water in which the Na concentration reflects near-surface weathering reactions.

Potassium and Chlorid

The linear mixing trend for the saline samples in Figure 13A for mM of K plotted versus Cl fits the samples from the Big Branch Aquifer and the Baton Rouge sands. The samples from the coastal Pleistocene aquifers in the figure have more scatter and higher K concentrations and do not form a linear mixing trend. The linear trend in Figure 13A splits into two trends in Figure 13B in which the molar K/Cl ratio is plotted against the reciprocal of Cl concentration. The trends indicate the dilute waters in the Baton Rouge sands are slightly enriched in K (for unknown reasons) relative to those in the Big Branch Aquifer. The samples in Figure 13B from the coastal Pleistocene aquifers have higher molar K/Cl ratios and have too much scatter to define a linear mixing trend. However, with increasing chlorinity, the molar K/Cl ratios of all samples converge towards a common intercept in Figure 13B ranging from 0.0015 to 0.003, bracketing the ratio of 0.0029 for the average South Louisiana Miocene formation fluids (Collins, 1970). These ratios for the saltwater sources are more than a factor of six lower than in seawater. Removal of K from pore waters by illitization of smectites is a common diagenetic reaction in deeply-buried formations (Stoessell and Moore, 1983), making the ratio consistent with the saltwater source being a deep formation fluid.

Other Groundwater Constituents

Only minor to trace concentrations of Mg and SO_4 are present in the groundwater samples, consistent with the saltwater source coming from dissolution of halite by a formation fluid. However, the lack of SO_4 is not diagnostic because it is removed by both biogenic SO_4 reduction at near-surface temperatures and by thermal SO_4 reduction at higher temperatures. But the low concentrations of Mg support the saltwater source being a deep formation fluid. Mg is expected to be removed at higher diagenetic temperatures by dolomitization of calcium carbonate and transformation of

kaolinite and other 7A clays into 14A chlorite (Berner, 1971; Carpenter, 1978; Stoessell and Moore, 1983).

Age of Saltwater Source

The expected $\text{Sr}^{87}/\text{Sr}^{86}$ ratios for marine formation fluids range from 0.7089 in late Miocene to 0.7090 in Pliocene and to 0.7092 in Quaternary (Faure, 1998). The measured ratios of 19 out of 20 samples in this study are plotted versus the reciprocal of total strontium concentrations in Figure 14 with the one unplotted sample being off scale. The ratios are grouped by aquifer or group of adjacent aquifers and six mixing trends are shown in the figure. The mixing trends have to be used with caution because two trends involve only two samples each. Nevertheless, the intercepts provide an estimate of the expected ratios in the saltwater sources. These ratios range from 0.7080 to 0.7085, corresponding to seawater ages of Middle Oligocene to Early Miocene, consistent with the saltwater sources being older formation fluids than *in situ* marine fluids in the Late Miocene to Pleistocene-age aquifers. The negative slopes of some of the mixing trends are unexpected. We can only hypothesize that earlier saltwater sources were deeper (older) formation fluids and their lower isotope ratios are reflected in the brackish groundwaters.

Conclusions

A simple chemical profile of the formation fluids in deep Cenozoic Gulf Coast formations shows that they originate from the dissolution and other diagenetic reactions (Stoessell and Moore, 1983). The deep formation fluid brines have low molar Br/Cl ratios, molar Na/Cl ratios approaching one, low molar K/Cl ratios, and are depleted in SO_4 and Mg concentrations. A similar chemical profile was identified in this study and in Stoessell and Prochaska (2005) for the saltwater sources in the brackish waters in the shallow South Louisiana Aquifer System. The only known halite sources in the Gulf Coast Region are deep salt diapirs, suggesting the saltwater sources were deep migrating formation fluids. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios imply the minimum age of these formation fluids are Early Miocene; therefore, much older than *in situ* marine pore

water for South Louisiana Aquifer system that have a maximum age of the Late Miocene. The brackish fluids presently located within the South Louisiana Aquifer System are shown by the mixing trends to have dissolved halite from the deeper Louann Salt Formation. The deep formation brackish waters entered some of the shallow Upper Neogene and Quaternary aquifers by migrating up fault and then laterally encroaching updip due to hydrologic flow patterns typically associated with areas of high water withdrawal rates (Figure 15).

Unlike the Baton Rouge area and St Tammany, the saltwater encroachments in the coastal parishes are not associated with one specific regional fault system. The brackish specific conductivities in several of the well samples north of the saltwater aquifer fronts, indicate farther updip movement of the fronts is occurring, (e.g. CN-92 in the 200 ft sand; CN-86L in the 500 ft sand, CU- 767 in the 700 ft sand, VE-637L in the Upper Chicot Sand; SMN-108 in the Lower Chicot Sand, and OR-203 in the Gonzales Aquifer).

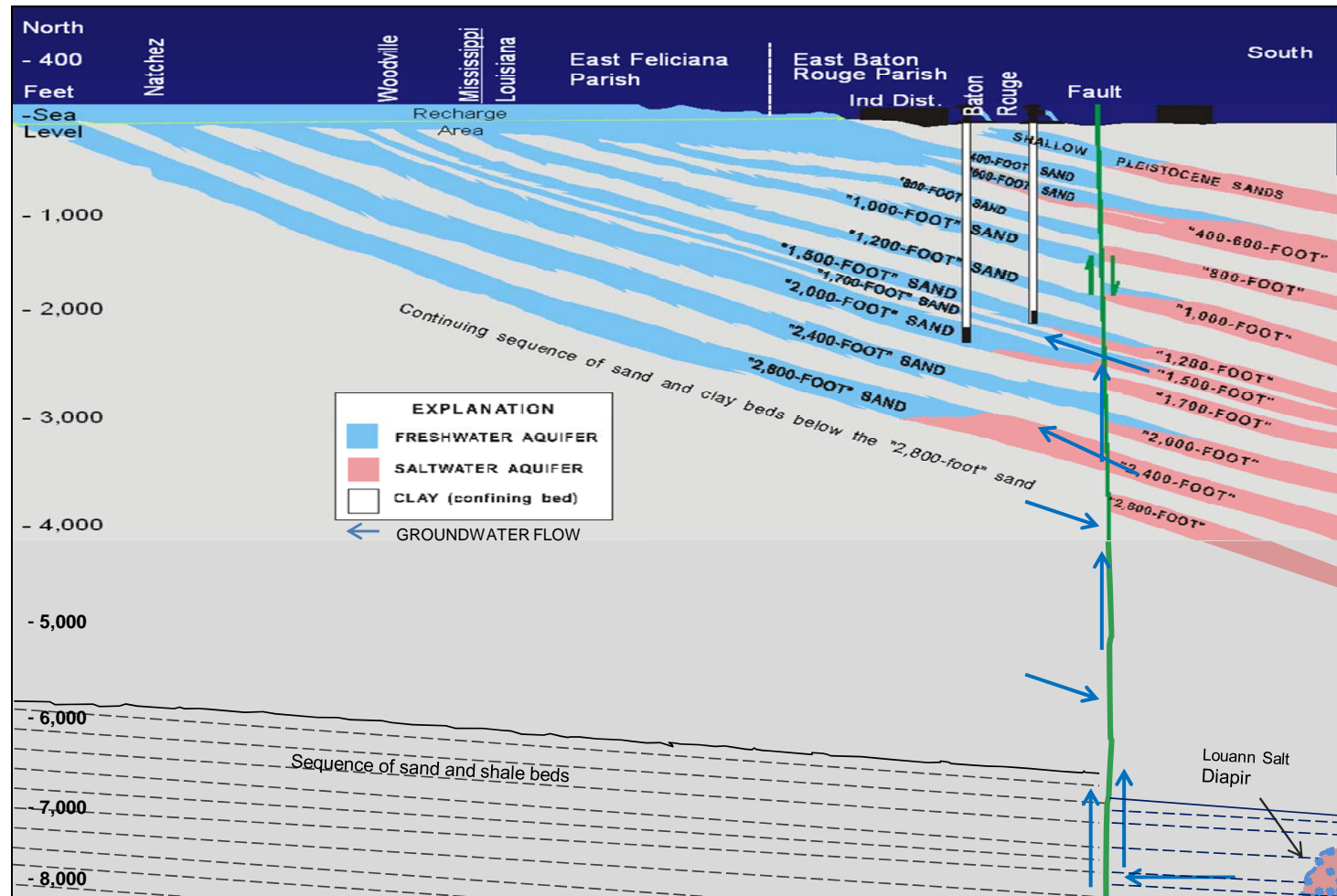


Figure 15: Revised idealized cross-section of Baton Rouge Aquifer System showing fresh water and saltwater locations. An alternative source of salt water are formation fluids in older formations, that have interacted with salt diapirs, entering the fault plane and moving updip into the shallow freshwater aquifers. The blue arrows show the groundwater movement and the green arrows show the relative displacement of strata across the fault. (modified from USGS, 2002).

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Vita

Lesley Cady Prochaska was born in New Orleans and raised in Chalmette, La. After high school Lesley attended the University of New Orleans pursuing a degree in Civil Engineering in order to design wetland restoration projects. After taking her first Geology class her sophomore year, Lesley decided to switch majors to Geology. As an undergrad, she was mentored by Dr. Patrick Shea Penland and Dr. Frank Hall. Dr. Penland hired Lesley as a student assistant for several years to assist with ongoing projects. Dr. Hall coached her in the application process for two undergraduate internships, one from the National Science Foundation and the other from the Student Conservation Association (SCA). Dr. Hall sponsored her undergraduate thesis Proper Functioning Conditions of the Gulkana River (Cady, 2000). During her internship with SCA in Alaska, she researched the geochemistry of a pristine river which led to her interest into geochemistry of groundwater.

After the completion of her undergraduate degree Lesley worked as an environmental geologist and obtained a Geographical Information Systems Certification from Penn State. She later continued her studies at UNO under the guidance of Dr. Ronald Stoessell, who opened her to the great world of geochemistry.