Interaction of Groundwater, Surface Water and Seawater in Wolf Bay, Weeks Bay, and Dauphin Island Coastal Watersheds, Alabama

by

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Abstract

Freshwater residing in coastal plain aquifers and watersheds represents one of our nation's most important natural resources. Globally, the distribution and fluxes of freshwater in many coastal settings remains poorly understood. As population, agricultural, and industrial centers have expanded along sea coasts, demands for freshwater resources have resulted in widespread water depletion and contamination in coastal regions. Integrative models rooted in science are needed to characterize surface water and groundwater quality and quantity in estuarine and coastal environments. This research used the Wolf Bay watershed, an EPA classified "Outstanding Alabama Water", and Weeks Bay, a coastal watershed with high-risk of mercury methylation, as a natural laboratory to gain an understanding of the hydrologic variables that affect water supply and water quality. To understand the hydrochemical conditions in which mercury methylates, water quality measurements of temperature, pH, oxidation reduction potential (ORP), dissolved oxygen (DO), turbidity, and electrical conductivity were collected at more than 60 locations in Wolf Bay and Weeks Bay. A bay cruise was conducted in July 2008 to sample bay water and measure water quality parameters. Major ion and stable isotope (oxygen and hydrogen) concentrations were analyzed in the laboratory to investigate the mixing of seawater and freshwater. The results indicated elevated concentrations of chloride (Cl) and sodium (Na) are high in bay water. Oxygen and hydrogen isotope analysis provides additional information on the degree of evaporation and water mixing in bays. Wolf Bay water is enriched in ^{18}O and ^{2}H relative to Weeks Bay water, river water, and shallow groundwater, indicating that its has received less freshwater input, or undergone greater evaporation and mixing with isotopically heavier seawater. In Weeks Bay high salinity seawater invades below acidic, low salinity water in the bay to form a wedge interface. Low DO and ORP values observed in this mixing zone indicate high microbial activities that may initialize Hg methylation. In Wolf Bay, by contrast, less freshwater inflow produces high salinity water, which may prevent key microbial processes that initialize Hg methylation and bioaccumulation. The results imply that Hg biotransformation is strongly influenced by hydrochemical conditions in coastal watersheds.

Regional scale groundwater flow models of southern Baldwin County were developed in a cross section extending from the northern recharge areas (near Bay Minette) to the Gulf Coast. The models predicted two flow regimes in major aquifer zones. Both local and regional flow regimes are present in Aquifer A2 due to local variations in topography and water table undulations. In the deeper Aquifer A3, a regional flow regime dominates in which flow directions are more consistent (i.e., from north to south) and controlled by the net topographic slope. Groundwater discharges southwards into the coastal estuaries (e.g., Wolf and Weeks bays) and Gulf of Mexico. Calculated groundwater flow velocities in major aquifers range from a few to tens of meters per year. The model calculated that groundwater residence time of major aquifers ranges from 0 near the recharge area to about 7000 years near the Gulf Coast

along a 70 km flow path. The calculated groundwater residence time is consistent with ^{14}C and ^{4}He ages measured by Carey et al. (2004).

Acknowledgments

Without grants from Gulf Coast Association of Geological Societies and the Alabama Geological Society, this study would not have been possible. I would like to thank Dr. Ming-Kuo Lee, Dr. James Saunders, Dr. Lorraine Wolf and Dr. Luke Marzen for their guidance and assistance throughout this project. The author would also like to thank Stan Mahoney and Rick Odess of the Wolf Bay Water Watch for their knowledge and use of equipment as well as Scott Phipps and Mike Shelton of the Weeks Bay National Estuary Research Reserve for allowing the use of their facilities and equipment. Finally, I would like to thank my family and friends for their support during my time at Auburn University.

Table of Contents

List of Tables

List of Figures

INTRODUCTION

Groundwater and surface water are a vital source of fresh water for industrial, municipal and private use. Globally and across the nation, the good stewardship of local watersheds is essential to the well-being of human communities and ecological systems within their boundaries (Alley, 1999). Alabama and the other southeastern states of the south Atlantic-Gulf region are the fastest growing areas in the United States. Thus, it is inevitable that water supply and quality problems will arise from population growth which underscores the need to protect water resources from degradation (Shat, 2005; Foster, 2006). Baldwin County lies along the Alabama Gulf Coast, an area where fresh groundwater is highly important due to the rapidly expanding development of the region and the subsequent increased water use (Chandler et al., 1985). The increasing use of water may cause overdevelopment of the groundwater resources, which in turn may cause water depletion, saltwater contamination, and other water quality problems. The lack of surface and subsurface data of the Wolf Bay watershed and the fact that it is an EPA Classified "Outstanding Alabama Water" (Alabama Water Watch, 2007) made this the perfect research area for this study.

Wolf Bay is located on the Gulf of Mexico in southern Baldwin County between Perdido Bay to the east and Mobile Bay to the west (Figure 1). Wolf Bay is an estuary where freshwater and seawater mix and its watershed host a diversity of habitats that support several federally listed species including black bears, bald eagles, Florida

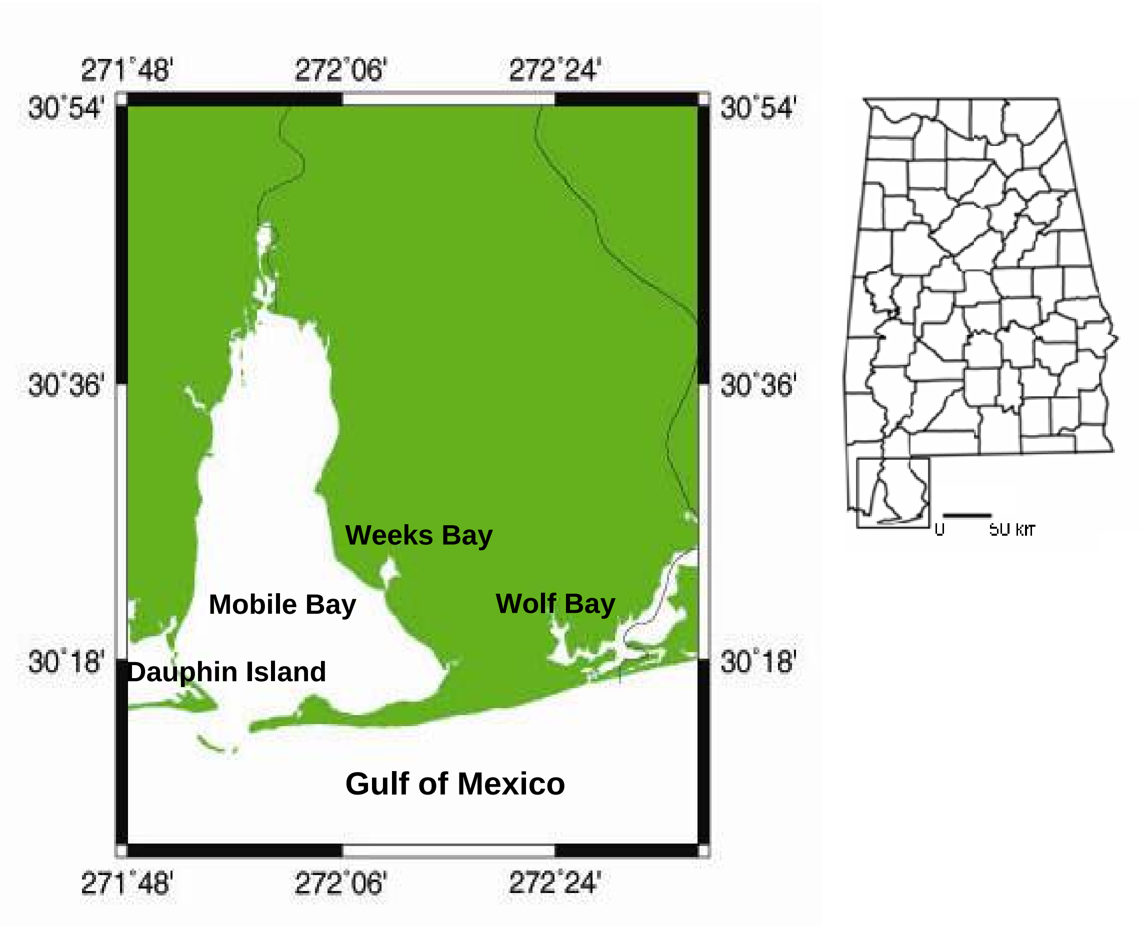


Figure 1: Site location map of Wolf Bay, Weeks Bay and Dauphin Island (modified from Monrreal, 2007)

manatees, sea turtles, Gulf sturgeons, red-cockaded woodpeckers, American alligators, Alabama red-bellied turtles, and Eastern indigo snakes (Alabama Water Watch, 2007). Major streams flow into Wolf Bay including Wolf Creek, Sandy Creek, Mifflin Creek, Graham Creek, Owens Bayou, Moccasin Bayou, and Hammock Creek. Wolf Bay flows into the Intercoastal Waterway, which flows into either Perdido Bay or Mobile Bay, depending on the moon, wind, and tide, and ultimately into the Gulf of Mexico (Alabama Water Watch, 2007).

Estuaries and coastal watersheds of Alabama Gulf Coast are highly susceptible to contamination by mercury (Hg), an element known to be extremely toxic to wildlife and humans. Weeks Bay, an estuary of Mobile Bay to the east of Wolf Bay, is located in southwestern Alabama's Baldwin County and has a watershed of 126,000 acres. Fish, such as Largemouth Bass, caught within the Weeks Bay watershed have been found to contain Mercury level above Federal Food and Drug Administration standards of 1 mg/kg. By contrast, fish consumption advisory related to Hg contaminated has not yet been issued in the Wolf Bay watershed. Although recent studies suggested that direct atmospheric deposition and riverine input are the primary sources of Hg to estuaries (Mason et al., 1994; 1999; Kim et al., 2004; Monrreal, 2007), the hydrologic controls on the fate and transformation of Hg in these estuaries remain poorly understood. The risks associated with mercury consumption coupled with the ever-increasing demand for water and seafood consumption underscore the necessity to understand the hydrology, water chemistry, and fate and biotransformation of mercury in Alabama coastal watersheds.

New tools are needed for accurate assessment of groundwater and surface flow conditions as aquifers are subjected to the stress of over-development and increased use. This is especially true in the Alabama Gulf Coast region, where increased development in local townships require dramatic land use changes and large quantities of groundwater from coastal plain aquifers. A hydrologic model is needed to accurately describe the characteristics of the groundwater watershed, the dynamics of basin-wide processes, and the impacts of anthropogenic (e.g. groundwater pumping) sources being put on the system.

The primary objectives of this study were to (1) measure spatial variations of water quality (i.e., temperature, conductivity, dissolved oxygen, oxidation-reduction potential) and chemistry (i.e. major ions, and oxygen and hydrogen stable isotopic compositions) in Wolf Bay and its major streamflows, (2) compile groundwater data (field parameters, major ions, residence time) to construct regional groundwater flow and hydrochemistry models, and (3) assess the freshwater/saltwater interfaces in the Wolf Bay and Dauphin Island areas using geophysical imaging methods involving the electrical resistivity measurements. The surface water measurements of Wolf Bay were compared to previous studies on Weeks Bay (Monrreal, 2007) to aid in the understanding of the hydrochemical conditions and key microbial processes that initialize mercury methylation and bioaccumulation in Alabama coastal watersheds.

Based on the data obtained from the research around the project areas this study defines surface water and groundwater quality and quantity (e.g., groundwater residence time and renewal rates) in the southern Baldwin County area; the data can be used to gain knowledge of the variables that affect water supply and water quality.

GEOLOGY AND HYDROGEOLOGY

Wolf Bay is located in southern Baldwin County, southwest Alabama and is in the Coastal Lowlands physiographic district which consists of saltwater marshes, swamps, bays, inlets, beaches, sand dunes, islands, peninsulas, and tidal waters (Chandler et al., 1996). The Bay is an estuary between Perdido Bay to the east and Weeks Bay to the west and has a watershed of about 44,700 acres (Alabama Water Watch, 2007). The mixing of freshwater and saltwater in Wolf Bay creates a diverse suite of hydrologic environments and rich ecosystems. Four major tributary streams that flow into the bay include Wolf Creek, Sandy Creek, Miflin Creek, and Hammock Creek. The watershed is surrounded by developing urban centers (i.e., Foley and Elberta) that host large industrial and agricultural activities, all of which are potential point and non-point sources of pollution. The average annual precipitation in the study area is about 162.6 centimeters. There are no major rivers flowing across the watershed, which extends from south of I-10 to the Gulf of Mexico. A fundamental characteristic of the Wolf Bay watershed is that overland flow during precipitation events is minimal and only a small percentage of precipitation is discharged to the surface streams. The majority of water infiltrates the subsurface aquifers immediately. However, the increasing impermeable land covers due to urbanization has reduced freshwater infiltration. Weeks Bay is located in southwestern Baldwin County off of Mobile Bay on the Gulf Coast coastal plain. The largest surface stream in the Baldwin County (i.e., Fish River) discharges into the Weeks Bay, suggesting that the Weeks Bay may receive more freshwater inputs than the Wolf Bay.

Groundwater is the major source of water for municipal, irrigation, and industrial use in southern Baldwin County (Chandler et al., 1996). The groundwater pumping rates increased six-fold from 7×10^6 gpd to 4.2×10^7 gpd from 1966 to 1995 due to an expansion of use in irrigation and the demands of growing population (Robinson et al., 1996). Water is produced (up to 1,500 gpm) mainly from sand and gravel layers of Miocene-Holocene coastal plain aquifers (Chandler et al., 1996).

The main aquifers, locally known as A2 and A3 (Figure 2), are composed of unconsolidated Holocene-Miocene sediments deposited in fluvial and shallow-marine environments. The details of groundwater migration, water-quality evolution along flow path, and residence time or renewal recharge rates in various parts of the watershed remain ambiguous. The ^{14}C and ^{4}He groundwater ages (or residence time) were estimated to be in the range of 375-7500 years (i.e., the time since recharge) in the A3 aquifer along flow path of 30 to 70 km (Carey et al., 2004). The groundwater residence time suggests that groundwater migrates from north to south at rates of about 1 to 15 m/yr and ultimately discharges into the Gulf of Mexico. Regional water table slopes also indicate significant groundwater discharges southward into several coastal watersheds (e.g., Weeks Bay, Wolf Bay).

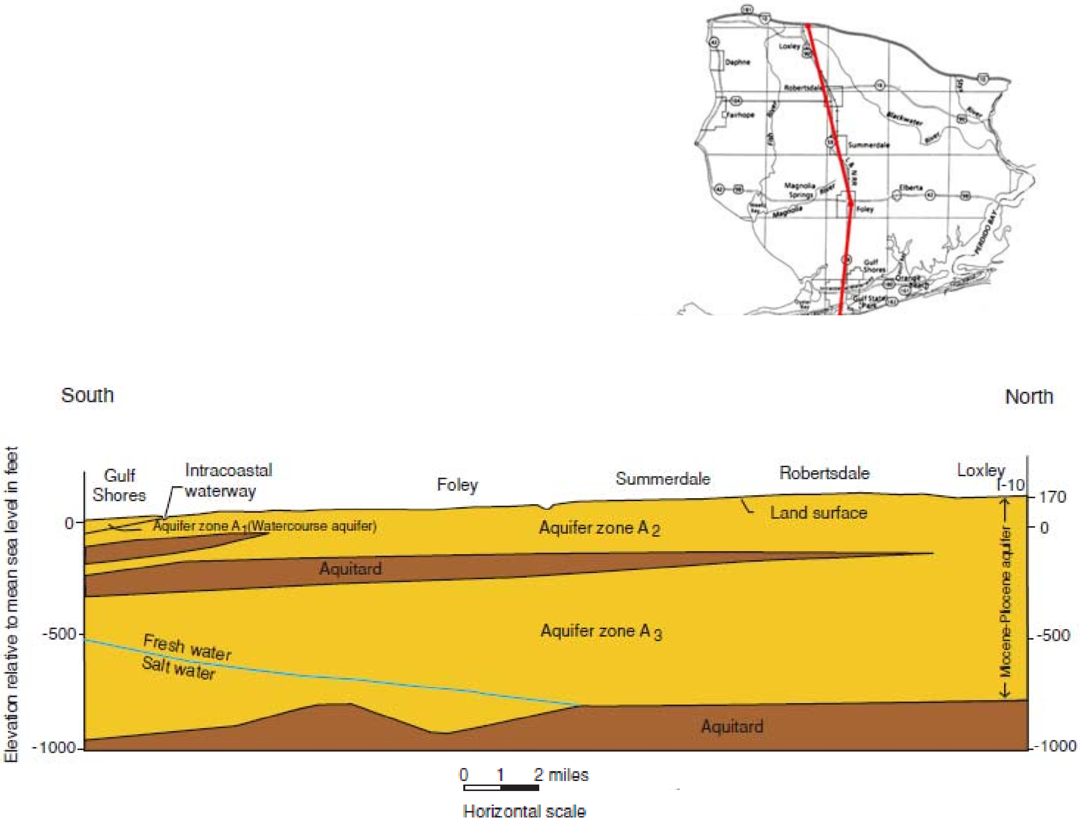


Figure 2: Hydrogeologic cross-section of southern Baldwin County, Alabama (modified from Chandler et al., 1985).

Hydrogeology of Southern Baldwin County

Geologic units that crop out in the study area range in age from Tertiary to Quaternary (Figure 3) (Mooty, 1988). The Tertiary age sedimentary deposits are generally unconsolidated and the alluvial and terrace deposits of Quaternary age overlie the Tertiary age deposits in and adjacent to the floodplains of the larger streams and rivers, and along the coastal areas of the Gulf of Mexico (Mooty, 1988).

The stratigraphy of southern Baldwin County as well as that of coastal and offshore Alabama consists of a relatively thick sequence of Jurassic to Holocene sedimentary rocks (Chandler et al., 1985). The middle Miocene to Holocene sedimentary rocks consist of interbedded sands, silts, gravels, and clays at relatively shallow depths, and host the freshwater aquifer zones in the Baldwin County area (Figure 4). These sediments thin towards the Gulf of Mexico and are part of three widely recognized geologic units defined by Reed (1971) as (1) the Miocene Series undifferentiated; (2) the Miocene-Quaternary Citronelle Formation; and (3) Quaternary alluvium, low terrace, and coastal deposits (Murgulet et al., 2008). The Miocene sediments are composed of white to light gray, fine to very coarse sands with some interbedded sandy, silty clay. The Pleistocene deposits have a greater abundance of interbedded sandy, silty clays as compared to the Miocene deposits. These deposits are overlain by sediments of Holocene age and consist of, white to pale-orange, fine- to coarse-grained sands, with some silt, clay, and shell hash (Chandler et al., 1996). These sediments are underlain by undifferentiated Eocene and Oligocene clays, sands, and carbonates (Figure 4).

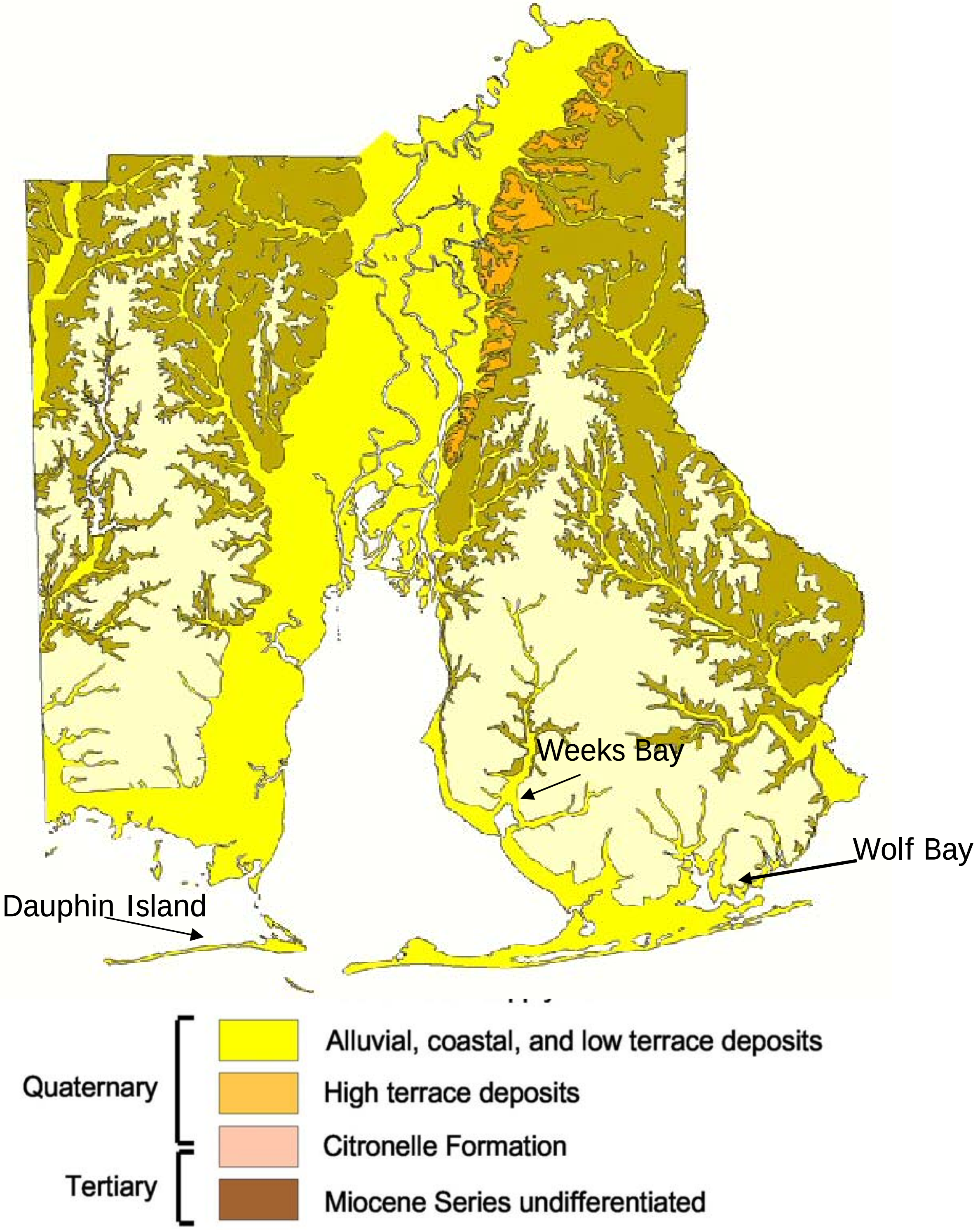


Figure 3: Geologic Map of the Wolf Bay area (modified from Mooty, 1988).

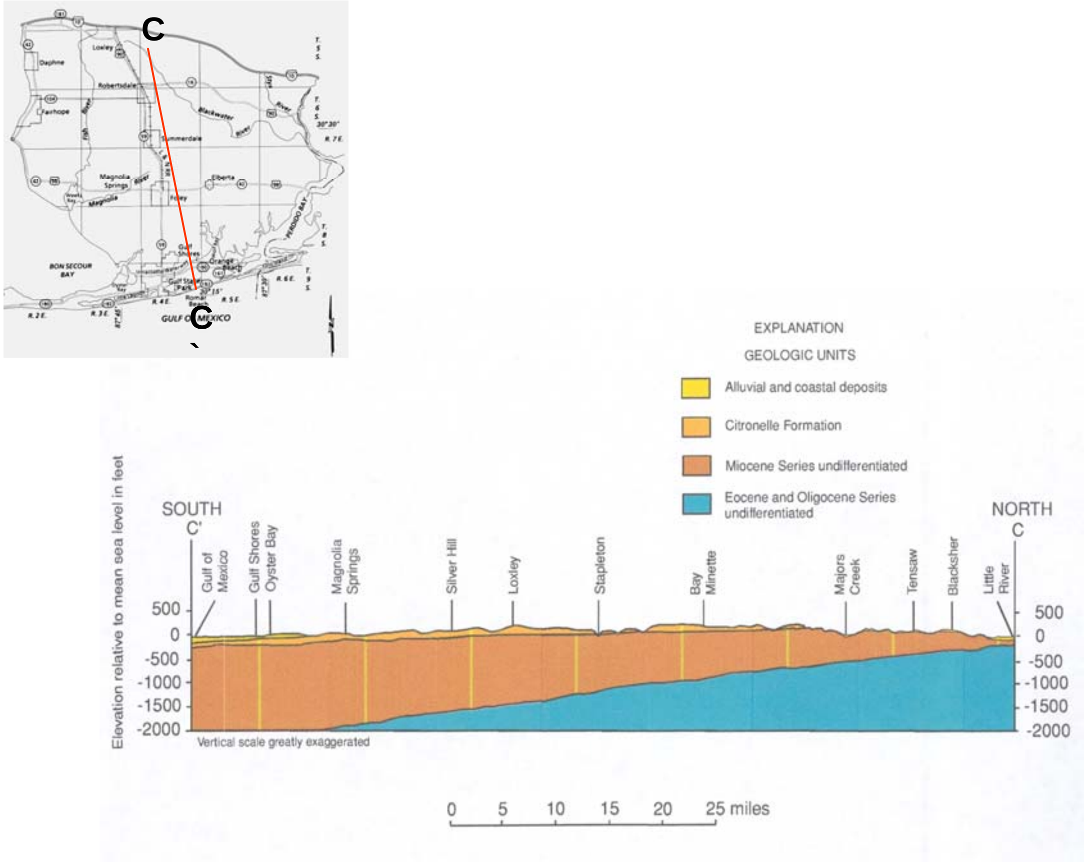


Figure 4: Generalized cross-section of southern Baldwin County (modified from Mooty, 1988).

Dauphin Island is located four miles off the southern end of Mobile County. It is a barrier island located between the Mississippi Sound and the Gulf of Mexico. The island is oval in shape on the east end, which is 1.4 miles wide and three miles long and narrows to 0.5 miles or less to the west extending approximately 12 miles. Dauphin Island is also located in the Coastal Lowlands subdivision of the southern Pine Hills District of the East Gulf Coast Plain section of the Coastal Plain province.

Three hydrogeologic units underlie Dauphin Island; the Deep Sand Aquifer, the Shallow Sand Aquifer, and the Water-Table Aquifer (O'Donnell, 2002). The Shallow Sand and Water Table aquifers are reportedly the only potential sources of fresh water on the island. Most of the island's surface lies very close to sea level and thus its freshwater resources are vey vulnerable to storm surge during major hurricanes.

The Deep Sand Aquifer is designated as Miocene sediments present at a depth of 500+ feet below sea level (O'Donnell, 2002). The deposit consists mainly of very fine to very coarse grain sub-angular to sub-rounded quartzose sand with shell fragments and traces of dark minerals with some clay and silt layers present.

The Shallow Sand Aquifer is composed of Miocene sediments between 150 and 500 feet below sea level and Pleistocene sediments between 50 and 150 feet below sea level and consists mainly of very fine to very coarse grain quartzose sand with some shell fragments, carbonized wood, silt and clay (O'Donnell, 2002). .

The Water-Table Aquifer, the top of which is visible at ground level on Dauphin Island, extends from ground level to the clay separating it from the Shallow Sand Aquifer (O'Donnell, 2002). The aquifer consists of well to moderately sorted, medium to very fine grained quartz sand, lenses of dark brown humate, silt, limonite, and streaks of semi-consolidated sands.

METHODOLOGY

Field Water Quality Data

The water data for assessing spatial changes in hydrologic and chemical conditions in the Wolf Bay watershed were recorded using a multi-parameter TROLL 9000. The lightweight, rugged TROLL 9000 is capable of monitoring up to 9 sensors simultaneously. Sampling was performed at 31 locations throughout the Wolf Bay (Figure 5). Parameters measured in this study include temperature, pH, specific conductance, dissolved oxygen (DO), oxidation-reduction potential (ORP), and turbidity. Data were recorded at 1-meter depth intervals until bay bottom sediments were reached.

Laboratory Geochemistry Data

In addition to the *in situ* water chemistry data, seven water samples were collected from directly above the bay bottom sediments for laboratory geochemical (major ions and oxygen and hydrogen isotopes) analysis. A Van-Dorn sampler was used to collect the water, which was then placed in 250 mL bottles and placed on ice before being shipped to the laboratory. These samples were sent to ACTLABS for major ion and trace element analyses using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Optical Emission Spectrometer (ICP-OES). Anion concentrations were measured by ACTLABS using Dionex 2000 Ion Chromatograph (IC). Stable isotopes ratios ($\delta^{18}O$ and $\delta\,^{2}H$) were determined using the standard CO_2 equilibrium method at the National High Magnetic

Laboratory at Florida State University. Results are reported in concentration units as permil deviations from the SMOW standard (Craig, 1961). Collectively, the results were used to assess the nature of mixing of surface water, groundwater, and seawater in Wolf Bay.

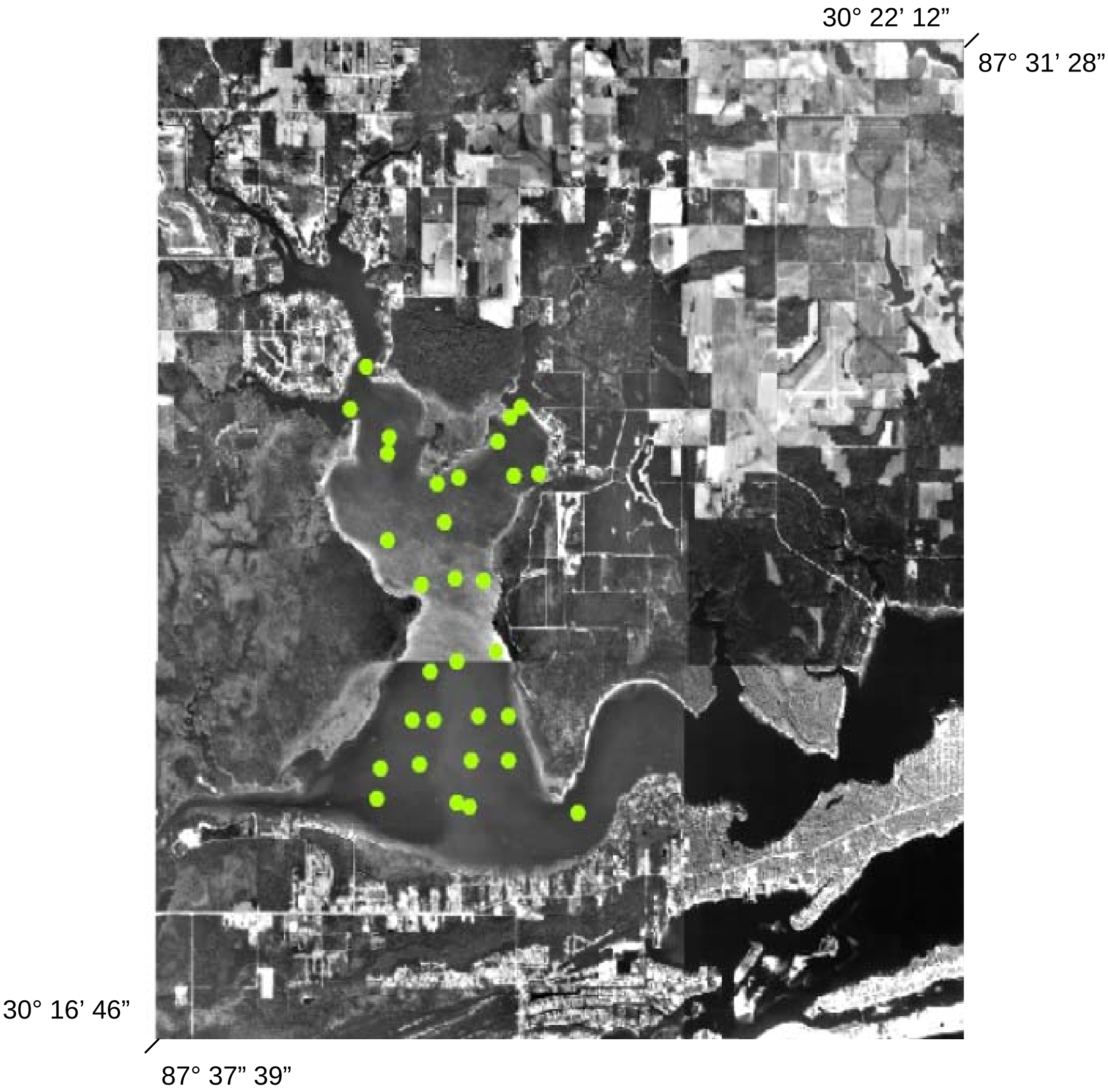


Figure 5: Sample location map in Wolf Bay, Alabama (aerial photos from alabamaview.org)

Geophysical Survey

Because of the limited knowledge of the freshwater/saltwater interface in the study area, a critical step in its comprehensive characterization should be to determine the salinity variation of groundwater. A geophysical survey using a 48-channel automatic switching resistivity system (Advanced Geosciences Super-Sting R-1) was conducted at Dauphin Island and Orange Beach, Alabama, that constitute shallow freshwater/saltwater interface (e.g. Al-Jahar et al, 2007, Swarzennski et al, 2007). Because bulk resistivity is most sensitive to variations in pore fluid properties (freshwater, saltwater, contaminants) the resistivity method was chosen to delineate the freshwater/salt water interface (Barlow, 2003). Two surveys were conducted. The first was on Dauphin Island, where shallow freshwater bearing wells were contaminated by Hurricane Katrina's storm surge. The other survey was conducted at Gulf State Park near Orange Beach, Alabama, and was compared to results from the Dauphin Island survey.

Groundwater Flow and Resident Time Modeling

The 2-D numerical models of groundwater flow and groundwater residence time were performed using basin-scale flow model *Basin2* (Bethke et al., 2003). Hydraulic properties (e.g., hydraulic conductivity and storage capacity) of aquifers and aquifers geometry and extent were compiled from literature (Sakr, 1999, Alley et al., 2002) for the modeling projects. The groundwater model was fully integrated with groundwater geochemical and isotope data. Calculated groundwater flow rates and residence time was calibrated against existing ^{14}C and ^{4}He isotope age data (Carey et al., 2004).

Geographic Information Systems (G.I.S.) models

A GIS base map was created using four combined aerial digital orthoquadrangles (DOQs) of the Wolf Bay area (alabamaview.org). Surface water sampling locations were plotted using the GPS measurements from the field. Spatial variations of water chemistry parameters within the bay were determined using 3-D Analyst in ArcGIS. The extent of Wolf Bay was clipped as a polygon and then interpolated into a surface map through the default kriging procedure to show the distribution throughout the bay at a 30m resolution. These maps were compared to find trends within the bay based on the differences in the field parameters.

WATER CHEMISTRY IN BALDWIN COUNTY AND DAUPHIN ISLAND

Well Locations and Specifics

The wells located in the North Well Field owned by the Orange Beach Water System (Figure 6) are developed in the A2 and A3 aquifers (Table 1). Riviera Utilities wells in Foley (Figure 6) are constructed in the Citronelle Formation and upper sands of the Miocene undifferentiated deposits which is recognized as the A2 aquifer, where the sand layers of these units serve as the aquifer for these wells (Table 2).

Dauphin Island Water and Sewer Authority’s wells #10, #20, #30, #40, #50, #60, #70 and #80 produce from the Water-Table Aquifer, which consists of well to moderately sorted, medium to very fine grained quartz sand, lenses of dark brown humate, silt, limonite, and streaks of semi-consolidated sands (O’Donnell, 2002) (Table 5).

Table 1. Riviera Utilities, City of Foley Well Locations and Well Specifics.

Riviera Utilities Well Locations (Foley, AL)			
Well I.D.	Latitude / Longitude	Well Depth (ft bls)	Screened Intervals (ft bls)
7	30.4047 / 87.6836	145	95-135
8	30.4036 / 87.6836	152	105-130 / 135-145
9	30.4080 / 87.6805	140	95-135
10	30.3705 / 87.6869	238	155-195
11	30.4038 / 87.6938	265	95-125
12	30.4108 / 87.6827	300	185-210

Table 2. Orange Beach Water, Sewer, and Fire Protection Authority well location and well specifics.

Orange Beach Well Locations (North Well Field)			
Well I.D.	Latitude / Longitude	Well Depth (ft bls)	Screened Intervals (ft bls)
Roscoe Well	30.3480 / 87.6508	326.4	220.05-235.38 / 260.46-296.15 / 306.15-326.40
Smith Well	30.3627 / 87.6580	352	205.21-245.89 / 281.03-306.70 / 331.70-352.00
Holasz Well	30.3466 / 87.6633	332.1	179.63-199.98 / 203.98-234.68 / 260.68-332.10
Roper Well	30.3552 / 87.6283	247.5	165.59-206.93 / 221.93-247.50

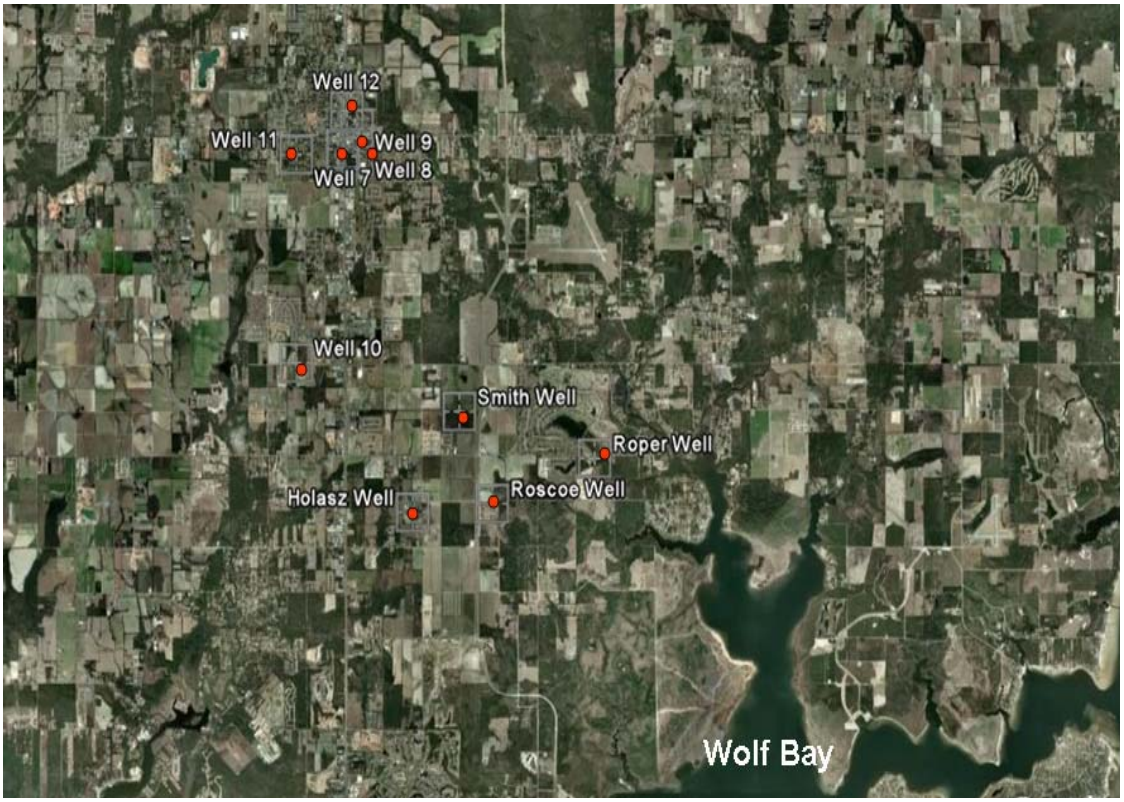


Figure 6: Distribution of municipal wells located in Foley and Orange Beach, Alabama.

Groundwater Geochemistry of Baldwin County

Groundwater chemistry data were collected from municipal wells managed by the Orange Beach Water, Sewer, and Fire Protection Authority, the City of Foley and Riviera Utilities, and from previous publications (Layne Geosciences, 1997; Goodwyn, Mills and Cawood, 2000) in the study area. Figure 6 shows the locations of these wells which were installed in the aquifer zones of A2 and A3. The physio-chemical parameters and major ion concentrations of the analyzed groundwater samples are shown in Tables 3 and 4. According to the relative molar proportion of the dissolved ionic species, the groundwater in the A2 and A3 aquifers in the study area shows mixed nature (Ca-Mg-Na-K and Cl-SO_4-HCO_3 types) (Figure 7). The groundwater is composed of varying values of alkalinity (range: 4.1 to 29.2; mean: 16.65), Na (range: 2.89 to 5 mg/l; mean: 3.95), Ca (range: 0.78 to 15.2 mg/l; mean: 7.99), Mg (range: 0.55 to 1.86 mg/l; mean: 1.21), Cl (range: 3.9 to 9.09 mg/l; mean: 6.5), SO_4 (range: 3.73 to 12 mg/l; mean: 7.865), and variable pH (range: 4.2 to 8.58; mean: 6.39). These groundwaters in general have low ion concentrations; their isotope ages and residence time (see sections below) correspond to young groundwater of meteoric origin.

Table 3. Groundwater major ion data from the Riviera Utilities, City of Foley Wells

Riviera Utilities, City of Foley Production Wells Major Ions											
Analyte Symbol	**Ba**	**Mg**	**Ca**	**Na**	**Zn**	**Mn**	**Cl**	**Fe**	**SO_4**	**Alkalinity**	**pH**
Unit Symbol	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Wells 7 & 9	<0.05	1.86	15.2	4.31	0.15	0.05	9.09	<0.05	3.73	27	8.58
Well 10	<0.05	1.27	14	2.89	0.19	<0.01	5.48	<0.05	<0.05	29.2	8.07

Table 4. Groundwater major ion data from the Orange Beach Water, Sewer, and Fire Protection Authority.

Orange Beach North Well Field Major Ions											
Analyte Symbol	**Ba**	**Mg**	**Ca**	**Na**	**Zn**	**Mn**	**Cl**	**Fe**	SO_4	**Alkalinity**	**pH**
Unit Symbol	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
Smith Well	0.046	0.089	1.3	5	0.022	0.035	3.9	0.97	12	7.8	5.9
Holasz Well	0.024	0.55	0.78	5	0.02	0.01	5.9	0.076	7.8	2.1	4.2
Roper Well							6		5.4	4.6	5.1

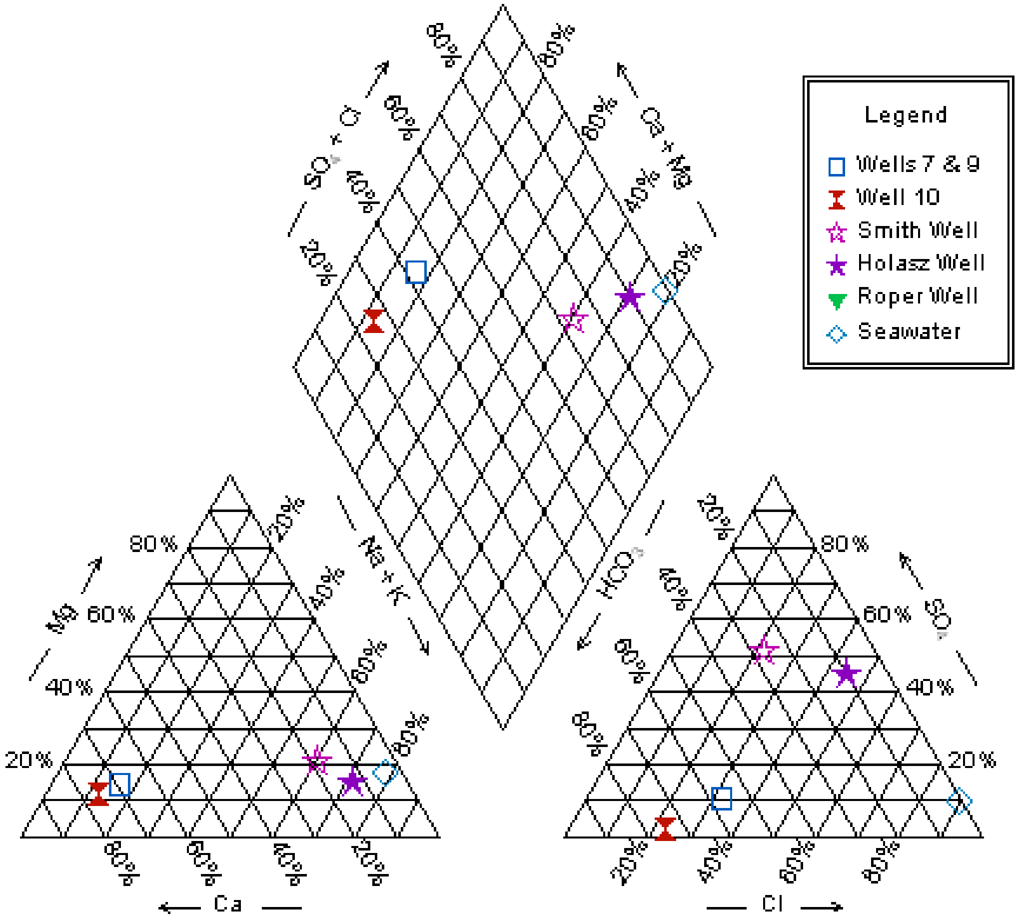


Figure 7: Piper diagram of drinking well water in southern Baldwin County.

Saltwater Intrusion in Southern Baldwin County

Previous study (Murgulet and Tick, 2008) conducted in southern Baldwin County on the A1, A2, and A3 aquifers showed that groundwater near the coastal margin possesses poor water quality with relatively high total dissolved solids (TDS), salinity, and chloride concentrations (Figure 8).

In the A1 aquifer elevated levels of TDS, salinity, and chloride were observed. The average salinity concentrations for aquifer A1 were 1,153.9 mg/L with a maximum of 18,000 mg/L in close proximity to the coastline (Murgulet and Tick, 2008). Chloride concentrations for the A1 aquifer were 486.2 mg/L with a maximum concentration of 7,758.3 mg/L in the Gulf Shores area. Average TDS concentrations were 1,359.3 mg/L with a maximum concentration of 14,590 mg/L (Murgulet and Tick, 2008).

The average salinity concentrations from the A2 aquifer was determined to be 96.8 mg/L with a maximum concentration of 2,590 mg/L and the average chloride concentrations were 28.2 mg/L with a maximum concentration of 1,460 mg/L (Murgulet and Tick, 2008). TDS concentrations averaged 146.8 mg/L with a maximum of 3,610 mg/L.

The groundwater samples obtained in the Murgulet and Tick (2008) study in the A3 aquifer exhibited relatively low concentrations of salinity and chloride compared to A1 and A2 aquifers. The average salinity concentration was 39.5 mg/L with a maximum

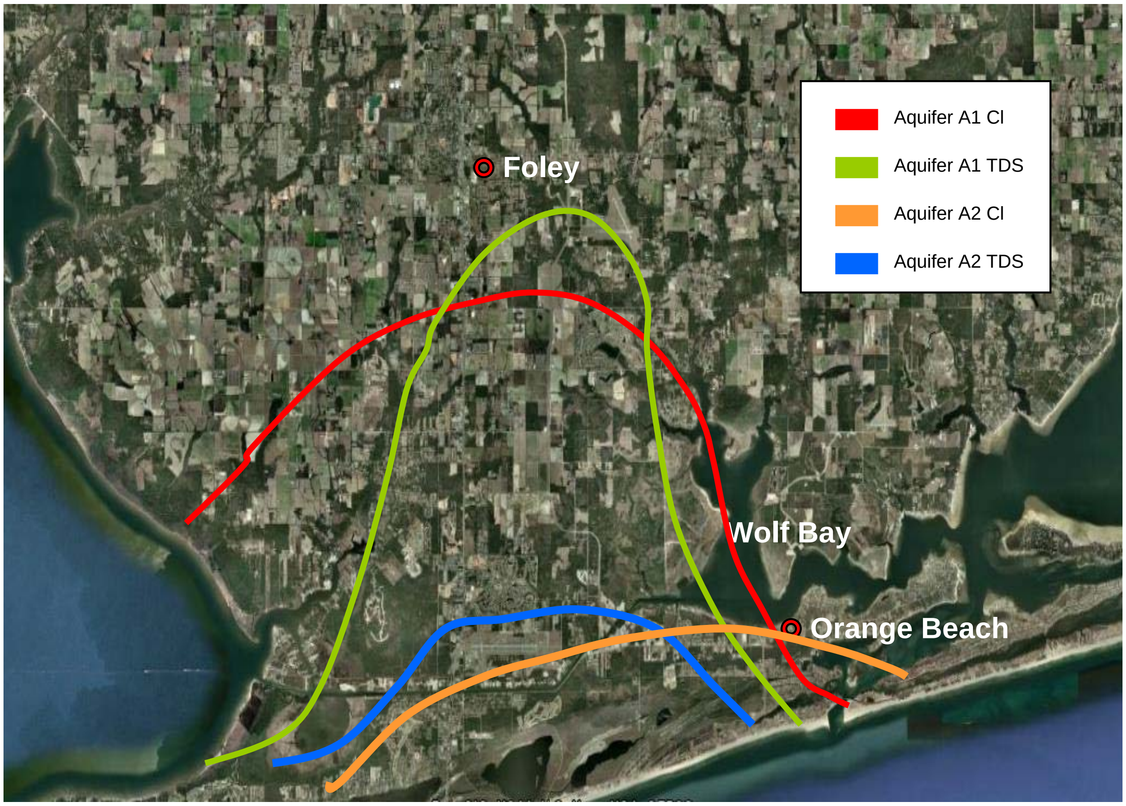


Figure 8: Contours show the positions of the chloride (250 mg/L) and TDS (500 mg/L) levels equivalent to drinking water limits set by the EPA (data from (Murgulet and Tick, 2008). These lines define the extent of saltwater intrusion occurring in the A1 and A2 aquifers in southern Baldwin County.

concentration of 136 mg/L and the average chloride concentration was 13.6 mg/L with a maximum concentration of 18.2 mg/L (Murgulet and Tick, 2008). TDS concentrations averaged 51.4 mg/L with a maximum of 190 mg/L north of the Intercoastal Waterway (Murgulet and Tick, 2008).

Results from the Murgulet and Tick (2008) study indicate that saltwater intrusion has occurred in the A1 and A2 aquifers, as indicated by high levels of chloride and salinity in wells completed near the Gulf of Mexico. The front of saltwater in the A1 aquifer, as defined by the 250 mg/L chloride isochlor, already approaches the inland area near Foley (Figure 8).

Groundwater Geochemistry of Dauphin Island

Data from Dauphin Island were received from the Dauphin Island Water and Sewer Authority. Dauphin Island currently has eight shallow wells in production. Chloride data was collected and Table 6 shows pre- and post- hurricane Katrina chloride levels in the wells. Table 7 shows the well locations and specifics of the shallow production wells.

Surface Water Chemistry of Wolf Bay and Weeks Bay

Data from the surface water sampling in Wolf Bay are shown in Table 7, which include latitude and longitude, temperature, pH, ORP, conductivity, DO, and turbidity from the July 2008 cruise survey. Measurements were taken at different depths to delineate the spatial distribution of the bay's water quality. The surface water near the Intercoastal Waterway (WB-1 through WB-10) is characterized by higher pH (7.75 to 7.93), higher temperature (29.05 to 31.72 °C) and high conductivity (32,990 to 36,050 µS/cm). In contrast, surface waters near the input of Wolf Creek (WB-24 through WB-31) into the bay have relatively lower pH (7.55 to 7.74), lower temperature (27.47 to 29.98 °C) and lower conductivity (22,980 to 33,800 µS/cm). The surface water sampled near the Wolf Creek mouth (where creek water mixes with bay water) has the lowest DO and ORP values (as shown in Table 7).

Table 5. Chloride levels in selected Dauphin Island wells pre- and post- hurricane Katrina (2005).

	Sep-03	Jul-06	Aug-06	Oct-06	May-07	
WELL #10	40	320	380	360	320	
WELL #20	25	180	200	180	140	
WELL #30	20	300	320		180	
	Jul-92	Sep-07	Aug-07	Oct-07	Dec-07	May-07
WELL #50	39	30	100	80	60	60
WELL #60	46	30	100	120	80	
WELL #70	48	30	60	80	60	60
WELL #80	26	30	50	100	80	80

Table 6. Dauphin Island Water and Sewer Authority well locations specifics.

Dauphin Island Water and Sewer Authority Shallow Production Wells			
Well I.D.	Latitude / Longitude	Well Depth (ft bls)	Screened Interval (ft bls)
#10	30.25380 / 88.11003	30	18-28
#20	30.25156 / 88.10153	32.5	20.5-30.5
#30	30.25124 / 88.9686	34.5	22.5-32.5
#40	30.25168 / 88.10746	33	21-31
#50	30.24913 / 88.10757	40	23.65-33.65
#60	30.24940 / 88.10377	40	24.75-34.75
#70	30.24767 / 88.09223	40	26.10-36.10
#80	30.24676 / 88.09223	40	26.65-36.65

For comparison, surface water data collected from Wolf Bay (this study) and Weeks Bay (Monrreal, 2007) are shown in Tables 7 and 8. In Weeks Bay, the river water and surface water near the river mouth are characterized by relatively low pH (5.99 to 6.54), low temperature (27.80 to 31.65 °C), and low conductivity (138 to 2017 µS/cm). The surface waters near the bay mouth however, have relatively high pH (7.8 to 8.75), high temperature (32.0 to 33.25 °C), and high conductivity (3350 to 5706 µS/cm). Conductivity of water in Weeks Bay is much lower than that in Wolf Bay. pH values of surface water in the upper Weeks Bay near the river mouth are also significantly lower. The surface water sampled near the river mouth where river water mixes with bay water has the lowest DO and ORP values generally. The major ion composition of surface water is shown in Table 9.

Table 7. Surface water chemistry from locations within Wolf Bay taken at surface level, collected in July, 2008.

Sample I.D.	Latitude	Longitude	pH	Conductivity	ORP	D.O.	Temperature	Turbidity
WB-1	30.1805	87.08734	7.92	36050	161	5692	31.72	12.8
WB-2	30.1807	87.34482	7.93	35000	176	6644	31.2	11.2
WB-3	30.3015	87.58907	7.9	34220	71	7130	30.15	14.8
WB-4	30.3019	87.59952	7.8	32990	69	6972	30.27	13.4
WB-5	30.3049	87.59916	7.8	34360	26	7090	30.6	13.4
WB-6	30.3054	87.59403	7.79	34810	48	7149	31.65	10.1
WB-7	30.3058	87.58722	7.81	35090	66	7151	29.86	10.3
WB-8	30.3057	87.58235	7.74	34530	73	7568	29.05	11
WB-9	30.3102	87.58242	7.8	34590	81	7095	30.75	9
WB-10	30.3102	87.58625	7.75	35190	86	7122	30.88	7.5
WB-11	30.3098	87.59225	7.82	35030	103	6730	30.64	9.4
WB-12	30.3097	87.59503	7.75	34780	102	7025	30.21	8.7
WB-13	30.3147	87.59267	7.62	34840	121	7023	28.36	8.1
WB-14	30.3156	87.58917	7.65	34330	116	7110	29.54	7.7
WB-15	30.3166	87.58405	7.66	34120	125	6791	28.92	8.9
WB-16	30.3238	87.5858	7.5	34380	121	7228	27.27	6.2
WB-17	30.3239	87.58946	7.67	32780	127	6329	30.43	7.2
WB-18	30.3233	87.59389	7.74	32680	123	7160	28.35	6.7
WB-19	30.3277	87.59825	7.73	32750	81	6977	29.67	7.7
WB-20	30.3295	87.59083	7.78	32910	119	6937	29.58	8.2
WB-21	30.3342	87.58184	7.76	34070	121	6203	29.73	7.3
WB-22	30.3345	87.5787	7.79	34060	131	6362	27.59	7.1
WB-23	30.3412	87.58103	7.75	33570	104	6928	27.41	8.1
WB-24	30.34	87.58235	7.74	33800	112	7060	28.16	9.7
WB-25	30.3376	87.58406	7.72	33790	-23	6766	29.44	13.14
WB-26	30.334	87.58916	7.61	33580	60	5587	27.47	3.2
WB-27	30.3334	87.59186	7.66	33080	94	6866	29.48	10.6
WB-28	30.3363	87.59828	7.58	29420	97	7777	29.81	7.2
WB-29	30.3379	87.59815	7.59	29200	106	6750	27.81	7.2
WB-30	30.3408	87.60319	7.6	23660	97	6772	29.72	9.6
WB-31	30.3451	87.60119	7.55	22980	114	7463	29.98	7.8

Table 8. Surface water chemistry collected from locations within Weeks Bay and Fish River taken at surface level in July 2005 (from Monrreal, 2007).

Sample I.D.	Latitude	Longitude	pH	Conductivity	ORP	D.O.	Temperature	Turbidity
WB1-S	30.4133	87.8255	6.47	909	540	5950	30.93	22.4
WB2-S	30.40947	87.82658	6.41	942.6	609	5020	31.65	22.5
WB3-S	30.37686	87.8358	8.49	5700	533	6700	32.82	19.9
WB4-S	30.38289	87.8348	8.6	5522	467	7394	32.89	21.6
WB5-S	30.39041	87.8331	8.77	5174	493	8100	33.56	17.6
WB6-S	30.3981	87.83061	8.43	2715	384	6360	33.02	23.3
WB7-S	30.40286	87.82869	6.28	300	488	4455	31.5	19.8
WB8-S	30.40080	87.82963	6.6	1311	518	5498	32.16	19.7
WB9-S	30.40722	87.82736	6.38	204	502	6233	32.17	22
WB10-S	30.38963	87.81616	7	3000	457	5038	32.0	29
WB11-S	30.39219	87.82005	8.09	3975	432	6330	32.66	28.2
WB12-S	30.39319	87.82469	8.62	4002	381	7360	32.60	24.1
WB13-S	30.39389	87.82908	8.66	5136	365	6110	33.17	19.8
WB14-S	30.39525	87.83678	8.3	2340	356	6658	32.66	18
WB15-S	30.39685	87.84175	8.06	1865	361	7150	32.69	31
WB16-S	30.39091	87.84086	8.41	2880	344	6800	33.06	19.9
WB17-S	30.38669	87.84013	8.75	3350	327	7356	33.22	23.3
WB18-S	30.38302	87.83894	8.79	3255	324	7746	33.22	21
WB19-S	30.37844	87.83705	8.8	3436	330	7815	33.25	20.9
WB20-S	30.40122	87.83738	8.19	2108	290	7255	33.63	24.4
WB21-S	30.40672	87.83422	6.69	560	386	5369	32.72	26.2
WB22-S	30.41030	87.82988	7.03	1119	409	7150	31.99	29.9
FISH1-S	30.44500	87.80433	6.8	66.01	403	8851	31.4	9.9
FISH2-S	30.44272	87.80280	6.63	65.31	482	8805	31.54	9.5
FISH3-S	30.44361	87.80728	6.57	63.97	514	9043	30.2	10.7
FISH4-S	30.44083	87.81160	6.9	71.4	455	9210	31.98	13.1
FISH5-S	30.43600	87.81261	6.98	69.26	447	9500	31.83	12.9
FISH6-S	30.43563	87.81891	6.82	76.5	454	9540	31.65	15
FISH7-S	30.43130	87.82372	6.83	98.3	443	9140	32.17	13.9
FISH8-S	30.42750	87.82855	6.61	105.2	444	8600	31.97	14.6
FISH9-S	30.42411	87.82477	6.7	123.3	441	8659	32.50	15.6

Table 9. Major ion composition of surface water collected from Wolf Bay.

Analyte Symbol	**K**	**Mg**	**Ca**	**Na**	**S**	**Sr**	**Cl**	**Br**	**SO4**
Unit Symbol	mg/L	mg/L	mg/L	mg/L	mg/L	**µg/L**	mg/L	mg/L	mg/L
Analysis Method	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-OES	IC	IC	IC
WB-10	306	675	234	6830	536	3580	10600	< 10	1520
WB-14	282	625	215	6380	493	3320	11000	< 30	1520
WB-19	272	613	208	6130	489	3260	6800	26.1	949
WB-21	270	613	210	6150	483	3270	9750	< 10	1390
WB-23	262	595	206	5950	468	3250	10700	37.8	1510
WB-28	248	573	198	5800	455	3030	9870	35.9	1370
WB-31	267	608	208	6080	473	3230	10700	38.9	1490

DISSCUSSION

Water chemistry is an important factor in the methylation and bioaccumulation of mercury. Conditions are constantly changing especially in estuary environments and can affect the fate and biotransformation of Hg. Data collected from the previous studies conducted in Weeks Bay and this study in Wolf Bay reveal how the difference in the hydrodynamics of the bays affects water chemistry and mercury methylation. Water samples were also collected for isotope and chemical analysis to investigate how water mixing and evaporation affects the water chemistry in the watershed. From the collected field data, GIS-based computer models were created to help interpret the mixing of surface water and seawater and the degree of evaporation in the bays. The Wolf Bay data were compared to the Weeks Bay data and analyzed to help obtain a better understanding of the water mixing within the bays and how that affects the methylation of mercury.

Mercury Deposition and Precipitation

Mercury deposition data from the Mercury Deposition Network (MDN) site AL02 (Figure 9) (http://nadp.sws.uiuc.edu/mdn) were compared with USGS precipitation data from the same time periods reported in Monrreal (2007) to show possible correlations between mercury deposition and precipitation for the area near the Weeks Bay and Wolf Bay watersheds. Figure 10 shows that total mercury wet deposition increases with the amount of weekly atmospheric precipitation.

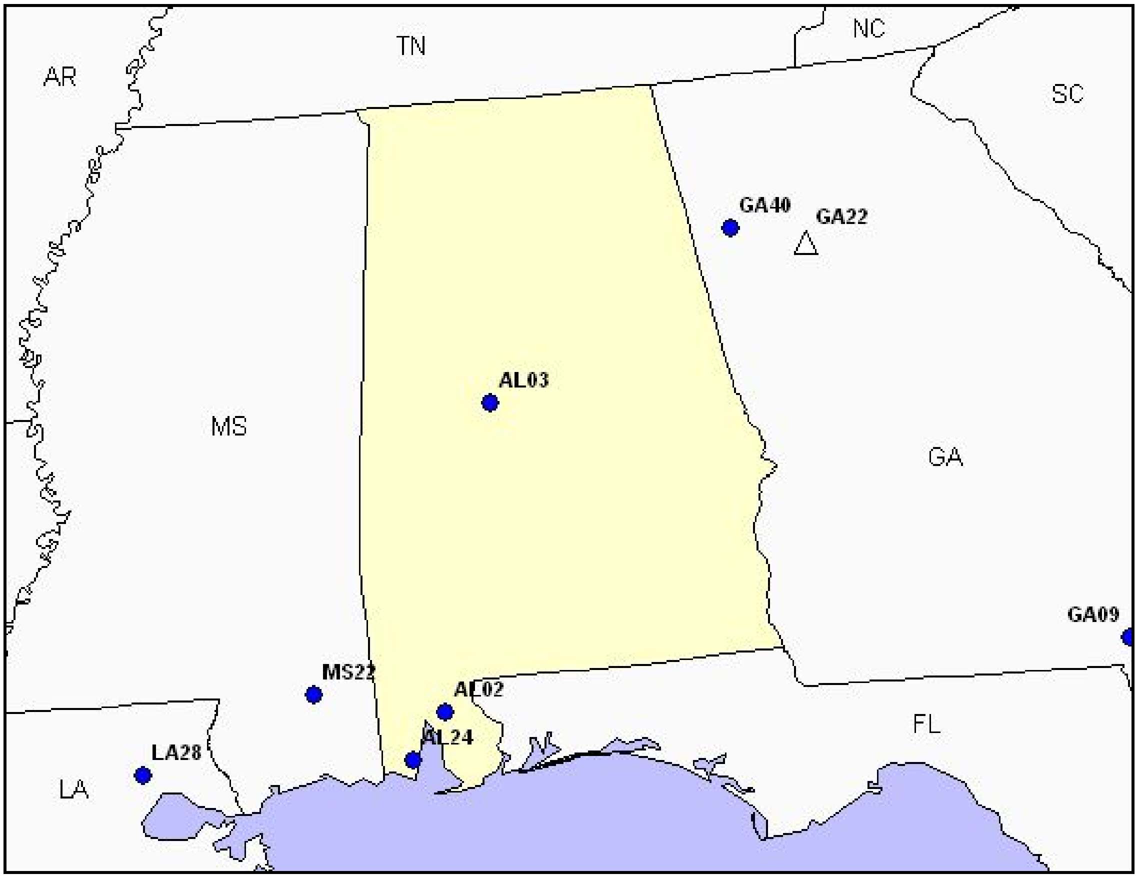


Figure 9: Map of location of MDN sampling sites in the southeastern region of the United States (http://nadp.sws.uiuc.edu). Data from sites AL02 were used for analysis of Hg deposition near Wolf and Weeks bays.

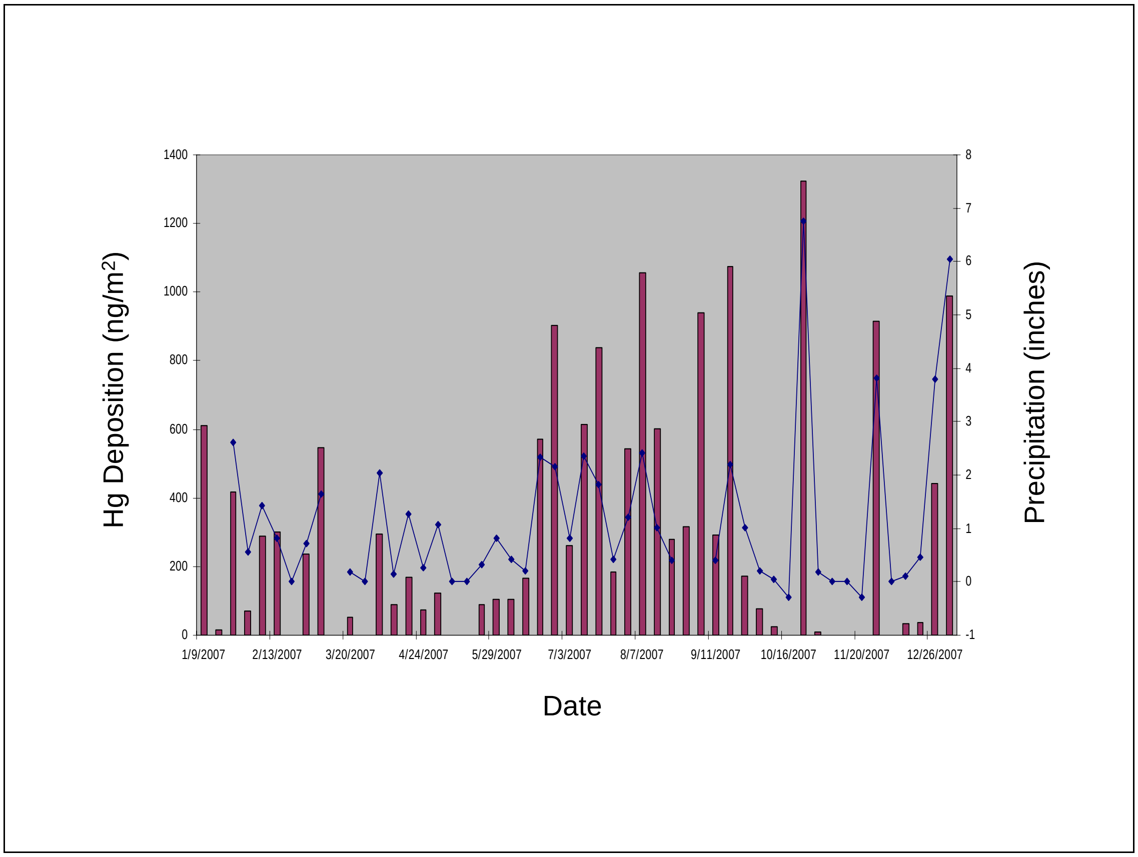


Figure 10: Fluctuations of total mercury wet deposition (collected by the Mercury Deposition Network, MDN) responding to rainfall in southwestern Alabama from January 2007 to January 2008. Rainfall data (vertical bars, in inches) were collected along the Fish River. The diagram shows increased mercury deposition during periods of higher precipitation, suggesting atmospheric deposition of mercury pollution.

The correlation of mercury wet deposition and precipitation data confirms that the likely source of mercury in Weeks Bay and Wolf Bay watersheds is atmospheric mercury deposition.

Surface Water Chemistry

Chemistry data of surface water demonstrates a mixing zone in Wolf Bay and Weeks Bay, resulting from seawater intrusion along the bottom of the bay. Grouping of different geochemical characteristics (Figures 11-14) indicate that those waters have distinct chemical characteristics, such as pH, conductivity, D.O., and temperature. Seawater has higher temperatures, pH, and electrical conductivity.

The chemistry data from the surface water samples show a mixing zone in Wolf Bay as a result of seawater intrusion along the lower portion of the bay. The geochemical analysis shows elevated chloride levels, which suggest that the bay has been contaminated by seawater. The intrusion of seawater into the bay creates a front of high salinity, high pH water that is denser and able to wedge underneath the lighter, low-conductive freshwater. Changes occur in water chemistry at the freshwater/saltwater interface and cause the bay to have pronounced stratifications due to the influx of seawater.

Each type of water has certain characteristics to fingerprint their origin such as pH, conductivity, D.O. and temperature. Mercury methylation favors waters with higher temperatures, lower pH, and lower salinity (or electrical conductivity). Surface water near the Intercoastal Waterway has the highest pH, temperature, and conductivity values. By comparing these parameters from Wolf Bay to Weeks Bay it may help to explain the spatial distribution of mercury methylation and its relation to the mixing of seawater, river water, and groundwater in the bays and the difference of the bays.

By comparing the data collected in Wolf Bay there appears to be a transition between the waters entering Wolf Bay from fresh water sources and that of the saline water in the bay itself. Measurements of pH and conductivity taken along a north-south transect from the mouth of Wolf Creek to the Intercoastal Waterway show a trend of high conductive, high pH seawater entering the bay (Figures 15 and 16). The data collected at lower depth have a higher pH and conductivity than those of the surface water. This trend suggests that the higher pH and higher conductive, denser seawater is intruding along the bottom of the water column in the bay and mixing with the lower pH and lower conductive waters from the creeks flowing into Wolf Bay. The pH, temperature and conductivity data collected at the surface and 1 meter depths in Wolf Bay also show the similar trend (Figures 17-20). Contour gradients of conductivity, temperature, and pH are more pronounced in the upper bay which indicates that a saline wedge has formed by the mixing of saltwater and freshwater. Waters at depth are more saline and warmer than those at the surface which is another indicator that dense seawater is intruding farther into Wolf Bay at depths below relatively fresher surface water. The plots illustrate that warm dense seawater invades beneath cooler fresh waters from the creeks that feed Wolf Bay. The saltwater wedge formed within Wolf Bay is indicated by the presence of the temperature and salinity stratifications. Previous studies in different watershed basins suggest that the highest mercury methylation primarily occur near the saline wedge, where lower pH water and low-salinity water are both present by mixing. The conductivity values in Wolf Bay (ranging from 22,980 to 36,050 μS/cm) appear to be much higher than those in Weeks Bay (ranging from 63.97 to 5700 μS/cm). This high salinity implies a less favored condition for Hg methylation (Ullrich et al., 2001; Celo et al., 2005; and Monrreal, 2007). pH values show greater variations in Weeks Bay than those in Wolf Bay, probably reflecting stronger mixing and freshwater inputs in the Weeks bay watershed.

The ORP and DO contour maps show areas of Wolf Bay that exhibit spatial variations in oxidized or reduced conditions (Figure 21). Some bacteria, such as sulfate reducing bacteria (SRB), prefer anaerobic waters with low ORP values that may contribute to the methylation of mercury (King et al., 2002; Monrreal, 2007). The lowest ORP values are located near the mouth of Wolf Creek, near the interface of fresh and brackish waters. Water DO and ORP values in Wolf Bay are comparable to those of Weeks Bay. However, in Weeks Bay low DO levels and reducing conditions prevail in the mixing zone near the mouth of Fish River. The reducing conditions in Weeks Bay may indicate more intensive microbial activity, which is an important factor in the methylation of mercury.

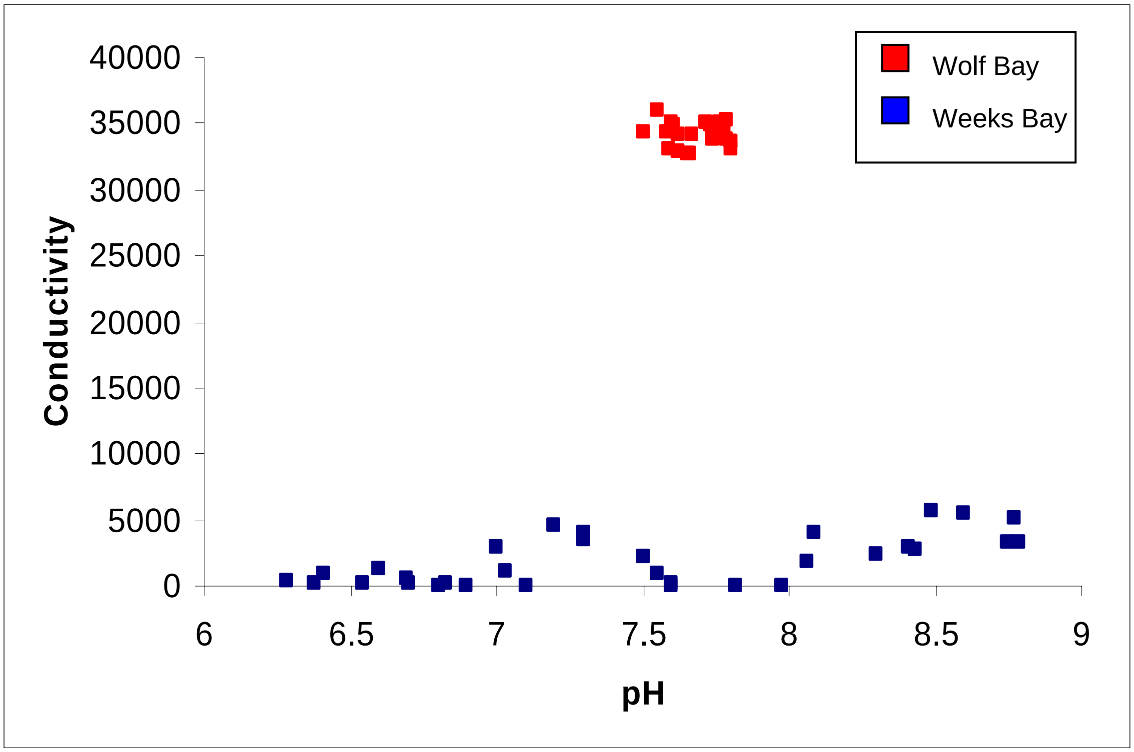


Figure 11: Plot of pH vs. conductivity showing a general relationship in water chemistry parameters that demonstrate the differences in the Wolf Bay and Weeks Bay waters.

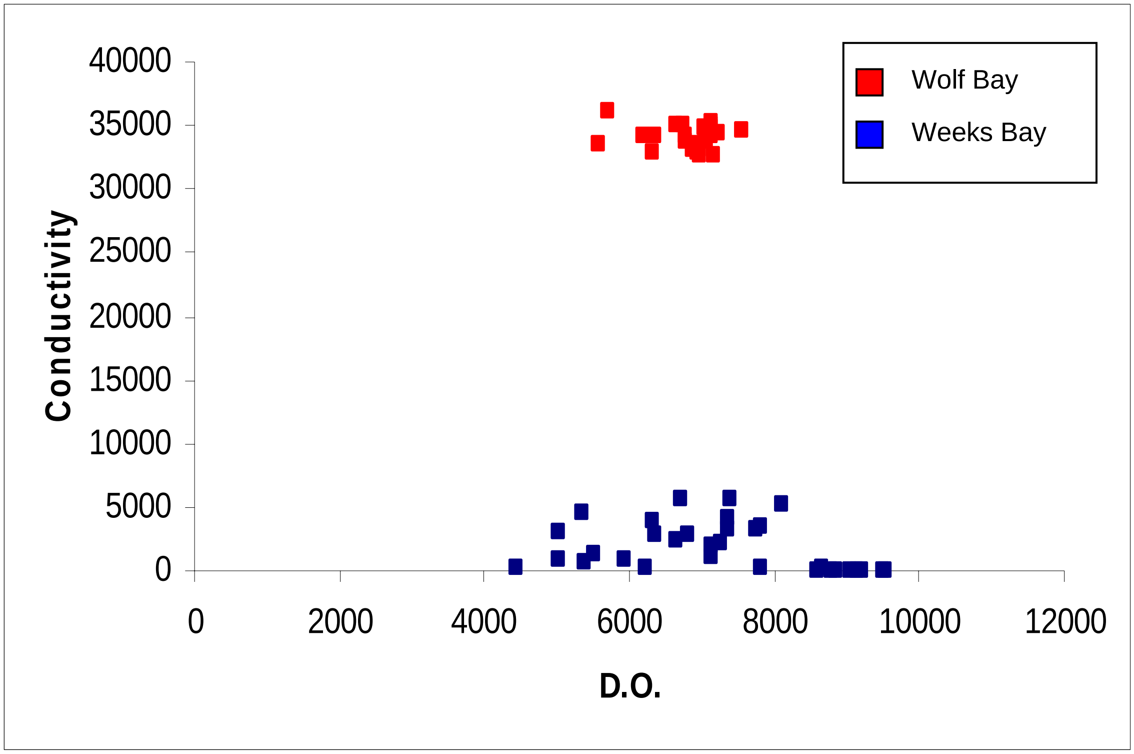


Figure 12: Plot of conductivity vs. DO comparing the water chemistry parameters from locations within Wolf Bay and Weeks Bay.

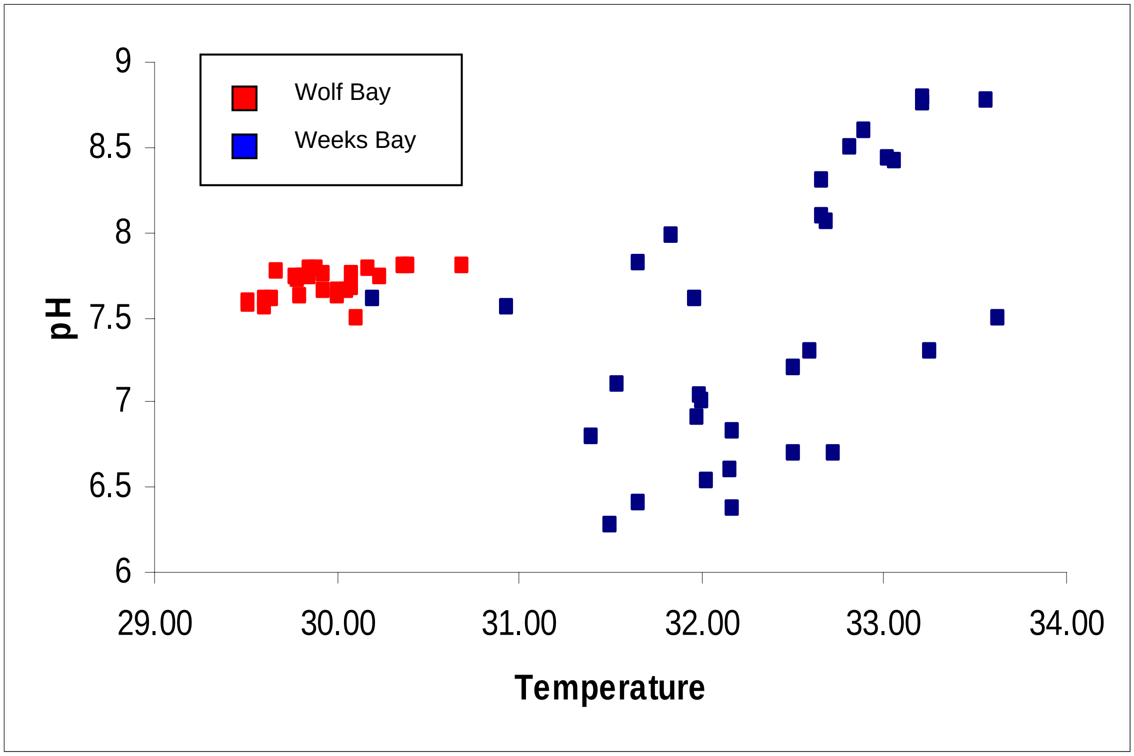


Figure 13: Plot of temperature vs. pH comparing the relationship in the mixing of the water within Wolf Bay and Weeks Bay.

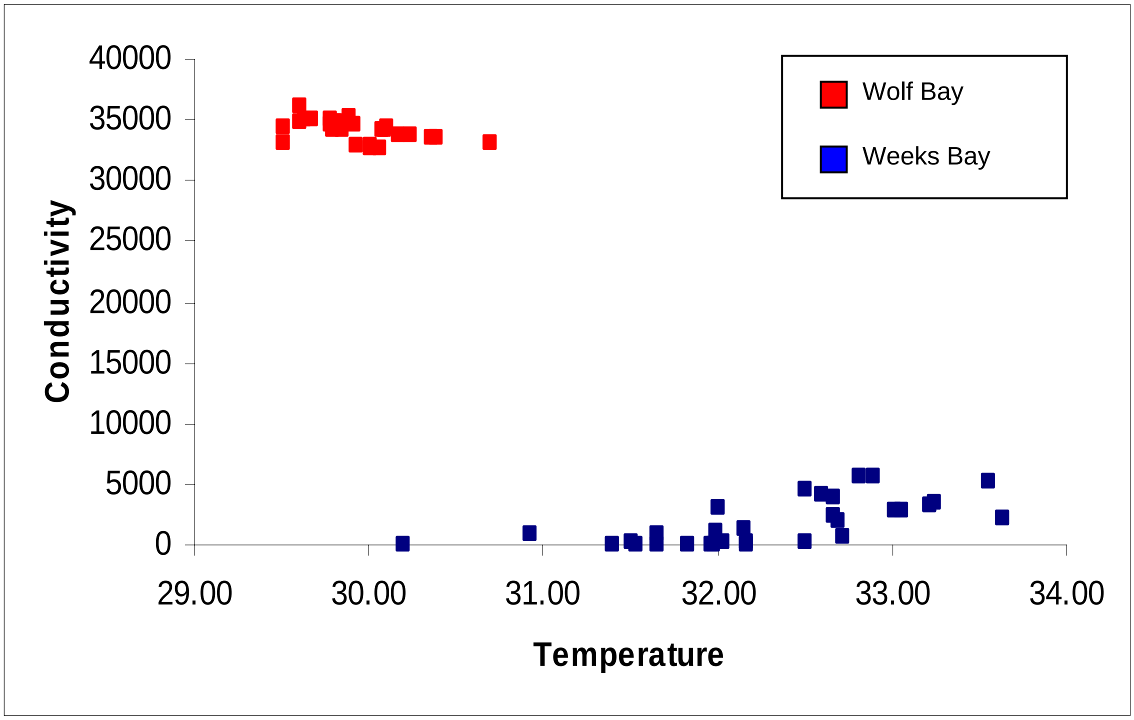


Figure 14: Plot of temperature vs. conductivity that compares the relationship between water chemistry within Wolf Bay and Weeks Bay.

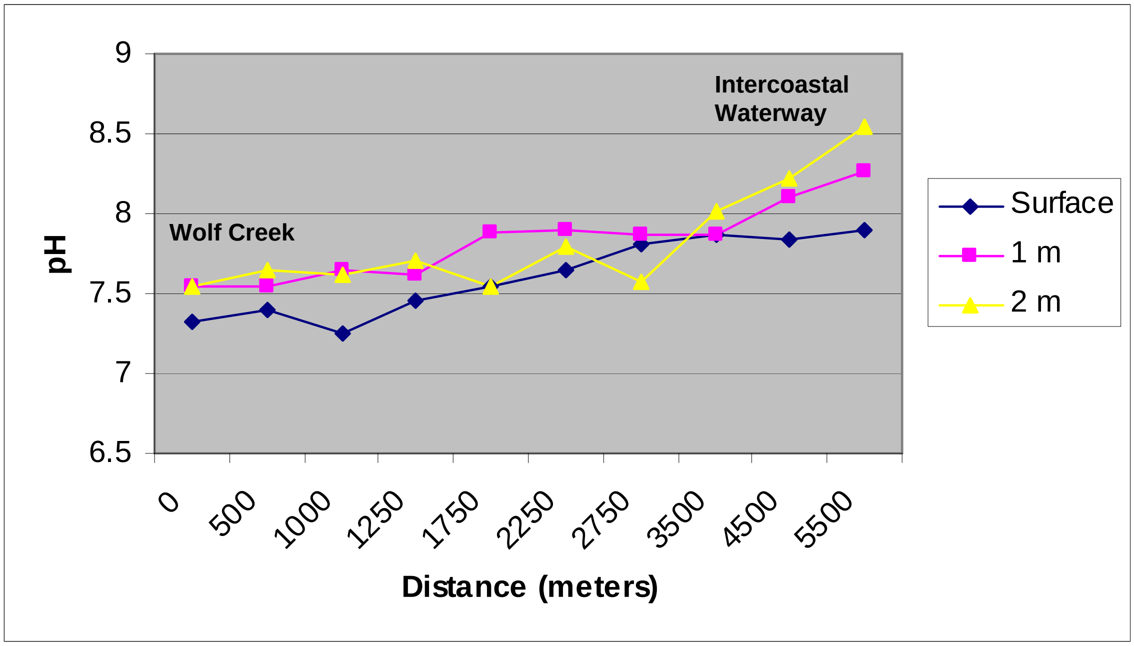


Figure 15: Plot of pH values at three different depths along a north-south transect from the mouth of Wolf Creek to the Intercoastal Waterway. The higher pH water is near the Intercoastal Waterway and the invasion of seawater into Wolf Bay creates a saltwater front.

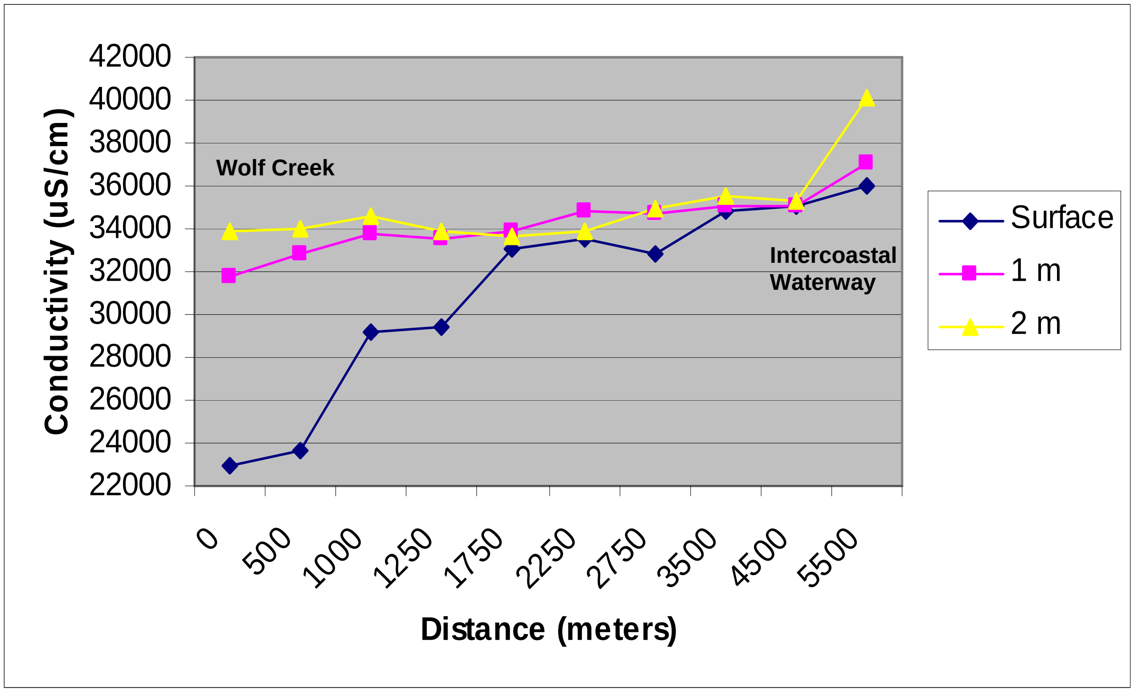


Figure 16: Plot of conductivity values at the surface along a north-south transect from the mouth of Wolf Creek to the Intercoastal Waterway. The increase in conductivity indicates a high salinity front which is created by the intrusion of seawater into Wolf Bay.

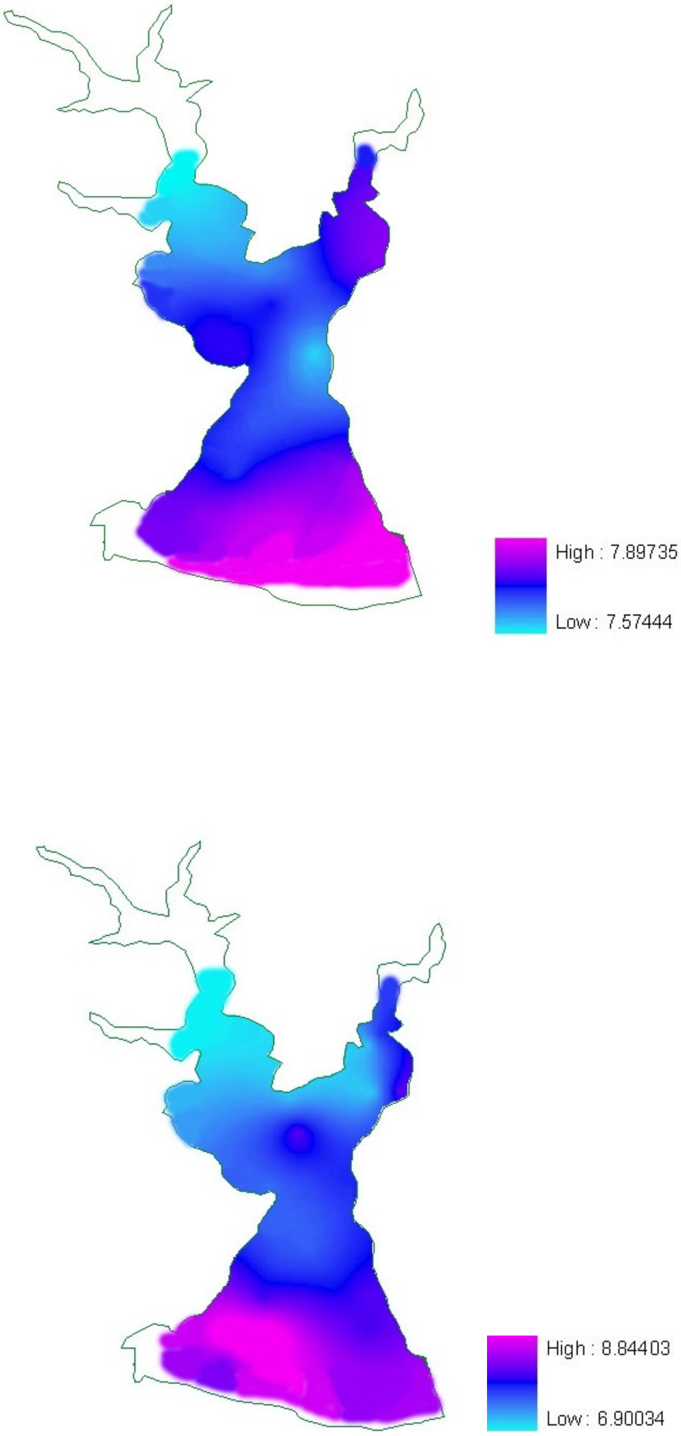


Figure 17: Contour map of surface (top) and 1-meter depth (bottom) showing pH levels in Wolf Bay.

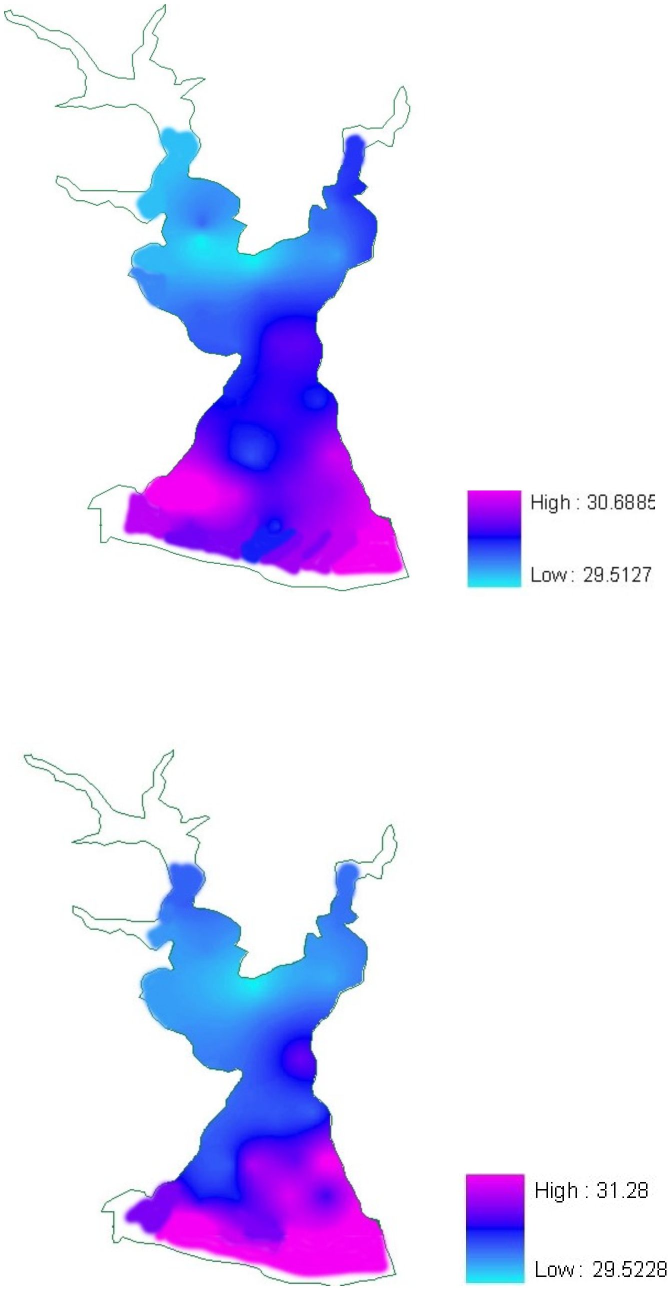


Figure 18: Contour maps of surface (top) and 1-meter depth (bottom) showing temperature (°C) levels in Wolf Bay. Like the pH readings, higher temperature water can be found closer to the Intercoastal Waterway.

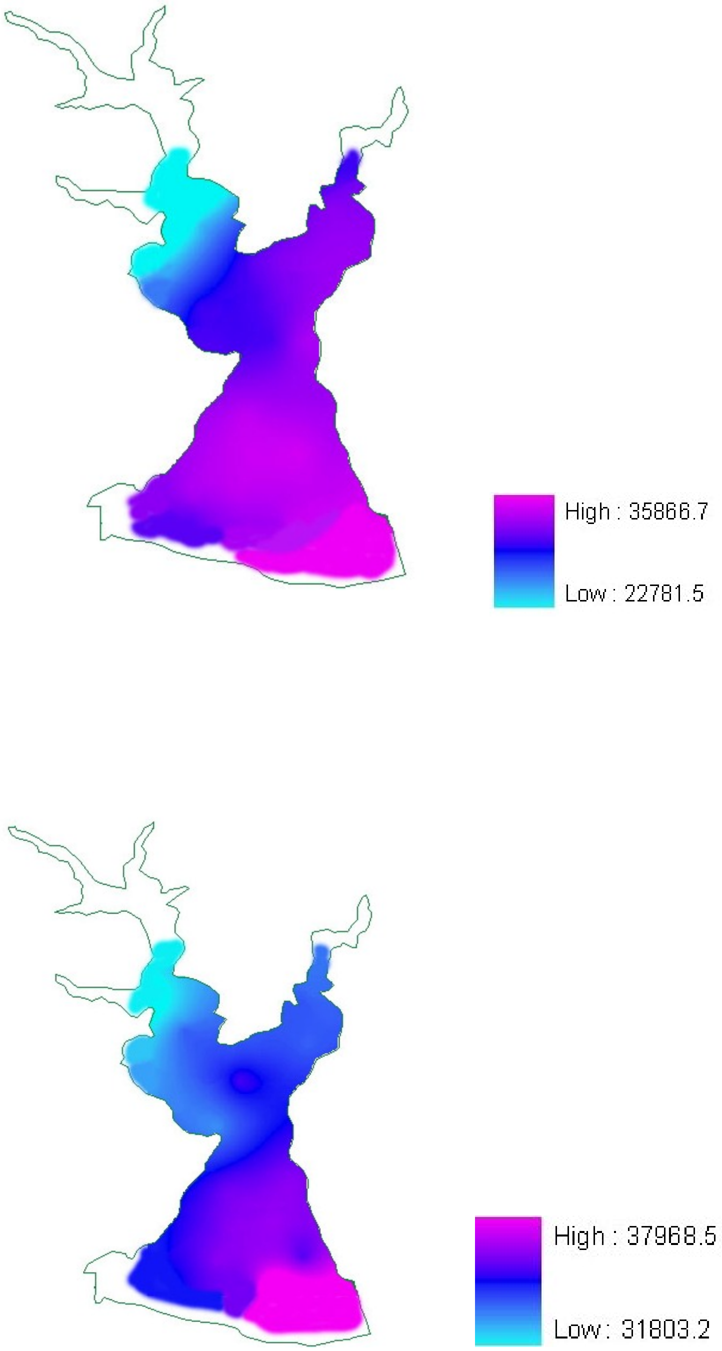


Figure 19: Contour map of surface (top) and 1-meter depth of conductivity levels (in µS/cm) in Wolf Bay. Similar to temperature and pH, higher conductivity readings can be found near the Intercoastal Waterway.

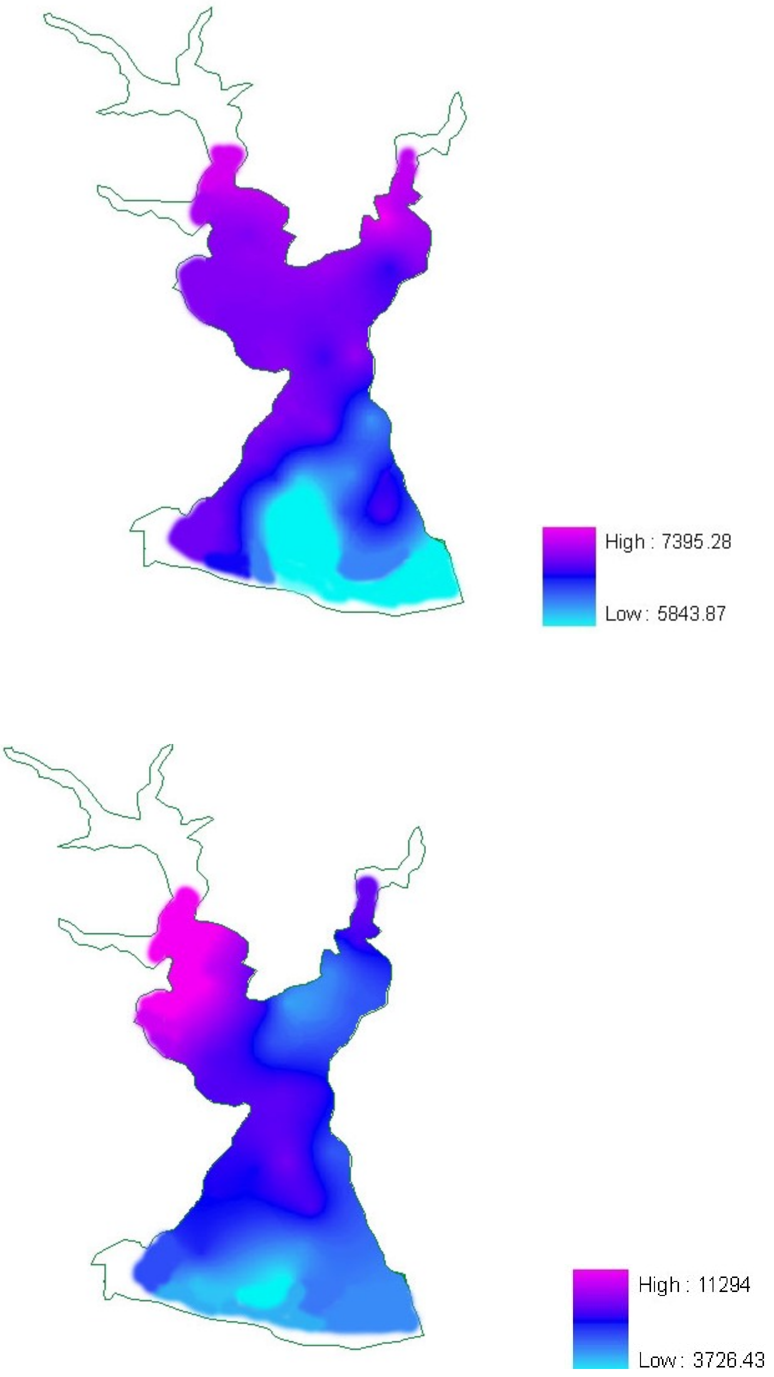


Figure 20: Contour map of (surface) and 1-meter depth of DO levels. The highest DO readings are located at the mouth of Wolf Creek.

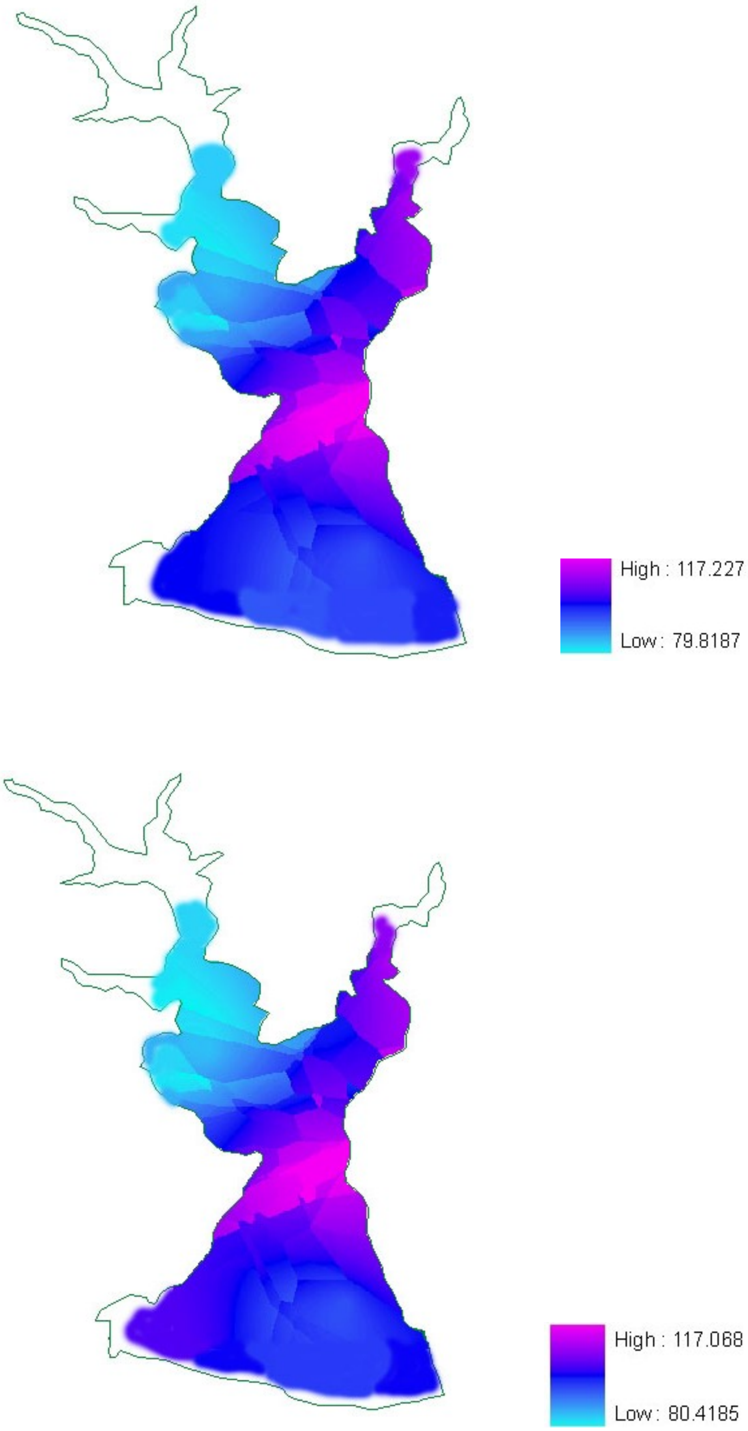


Figure 21: Contour map of surface (top) and 1-meter depth (bottom) of ORP. Lowest ORP zones are found at the mouth of Wolf Creek.

Figure 22 shows the geochemical characteristics of sampled waters in Wolf Bay and Weeks Bay using a piper diagram. The surface waters in Wolf Bay and Weeks Bay both contain high amounts of Na and Cl, similar to the characteristics of seawater. The Wolf Bay surface water has the same SO_4/Cl ratios (average 0.052) with respect to that of seawater (~0.052), suggesting that dissolved SO_4 in Wolf Bay has not been affected by bacterial sulfate reduction, a key process for initializing Hg methylation. By contrast, very low SO_4/Cl ratios are found in Weeks Bay where Hg methylation has occurred (Monrreal, 2007).

The groundwater analyzed from Weeks Bay contains high amounts of Na and HCO_3^- which indicates sodium bicarbonate type of groundwater. The Na-HCO_3 type high alkalinity of the groundwater in Weeks Bay is most likely a result of the combination of dissolution of calcite and ion exchange (Marimuthu, 2005; Penny et al., 2005; and Monrreal, 2007).

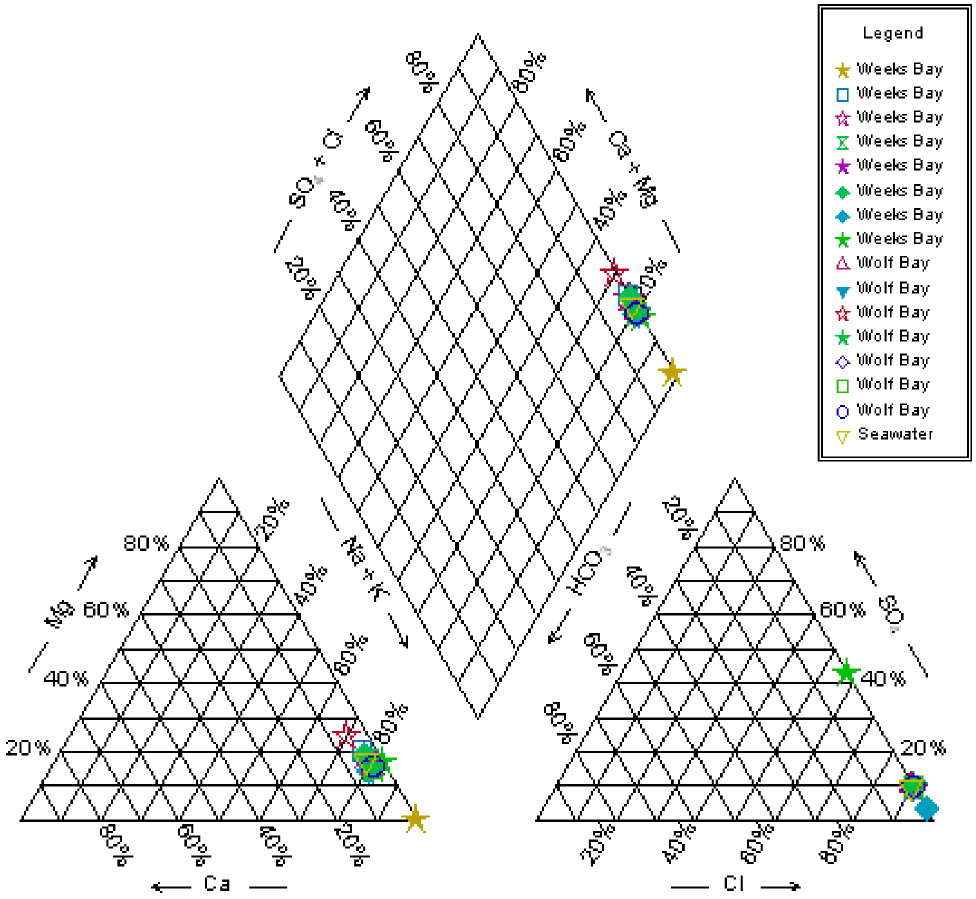


Figure 22: Piper diagram showing surface and groundwater compositions compared to that of seawater. Surface waters resemble those of seawater (i.e., Na-Cl types).

Major ion analyses can also aid in providing more information on the physical mixing and biogeochemical reactions that take place in the bays. Graphs were plotted to evaluate the mixing of the waters and compared to each other (Figures 23-26). In the plots, chloride, a conservative (non-reacting) species, is plotted on the x axis. The other species of interest, which may or may not be conservative, is plotted on the y axis. A straight line was drawn between the seawater and freshwater end-members and the behavior was based on the proximity of the data points to the line. If those data points lie close to or on the mixing line, that indicated the dissolved species exhibit a more conservative behavior. Data points that deviate significantly from the conservative mixing line are considered non-conservative. The species enrichment or depletion is in solution may be dependent upon biogeochemical processes such as mineral dissolution or precipitation, ion-exchange, or microbial processes.

In all of the graphs, linear trends reveal the conservative mixing between seawater and freshwater in Weeks Bay, while more non-conservative mixing can be found in Wolf Bay. Wolf Bay waters in general have higher major ion concentrations with respect to those in Weeks bay because of less freshwater inputs. The results of the graphical analyses indicate Na^{+}, Ca^{+2}, Mg^{+2} generally exhibit conservative behavior during mixing in Weeks Bay and less conservative behavior in Wolf Bay.

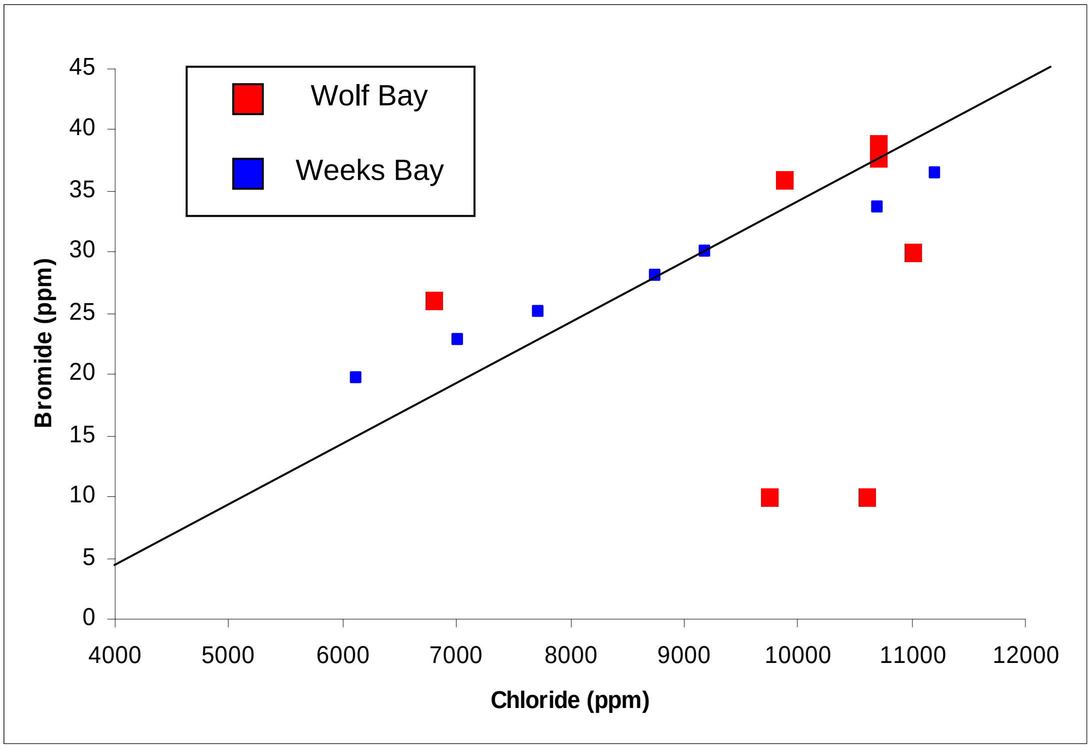


Figure 23: Plot of chloride vs. bromide showing a more linear pattern between the water in Weeks Bay and less in Wolf Bay.

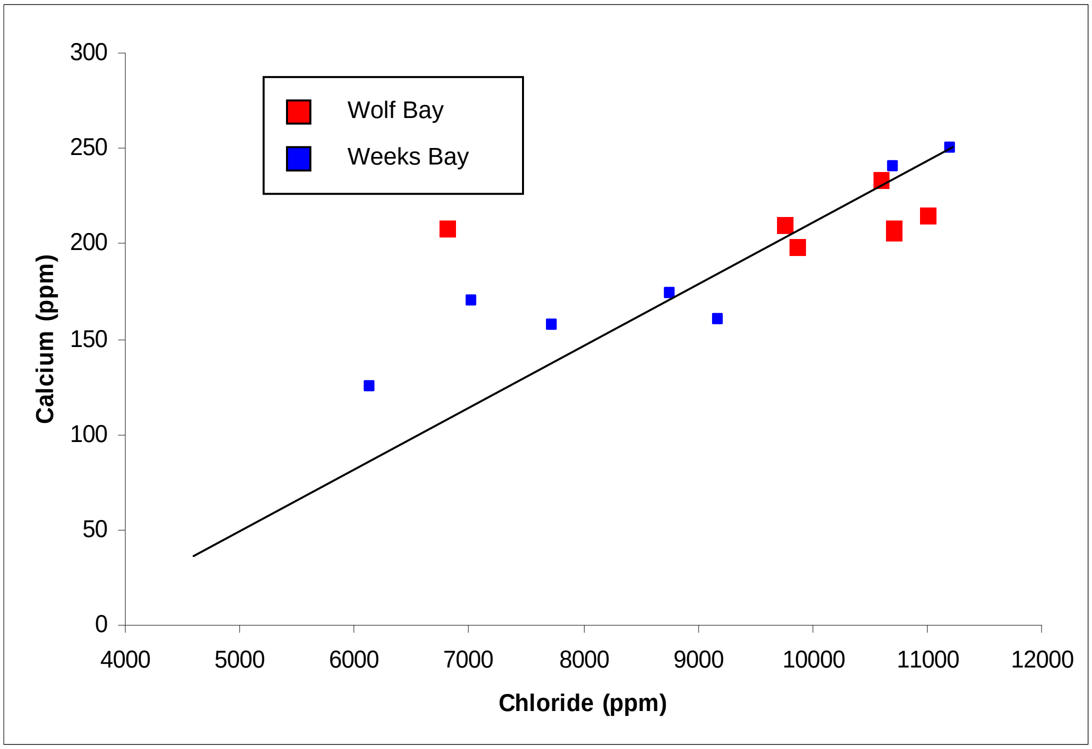


Figure 24: Plot of chloride vs. calcium showing similar patterns between waters.

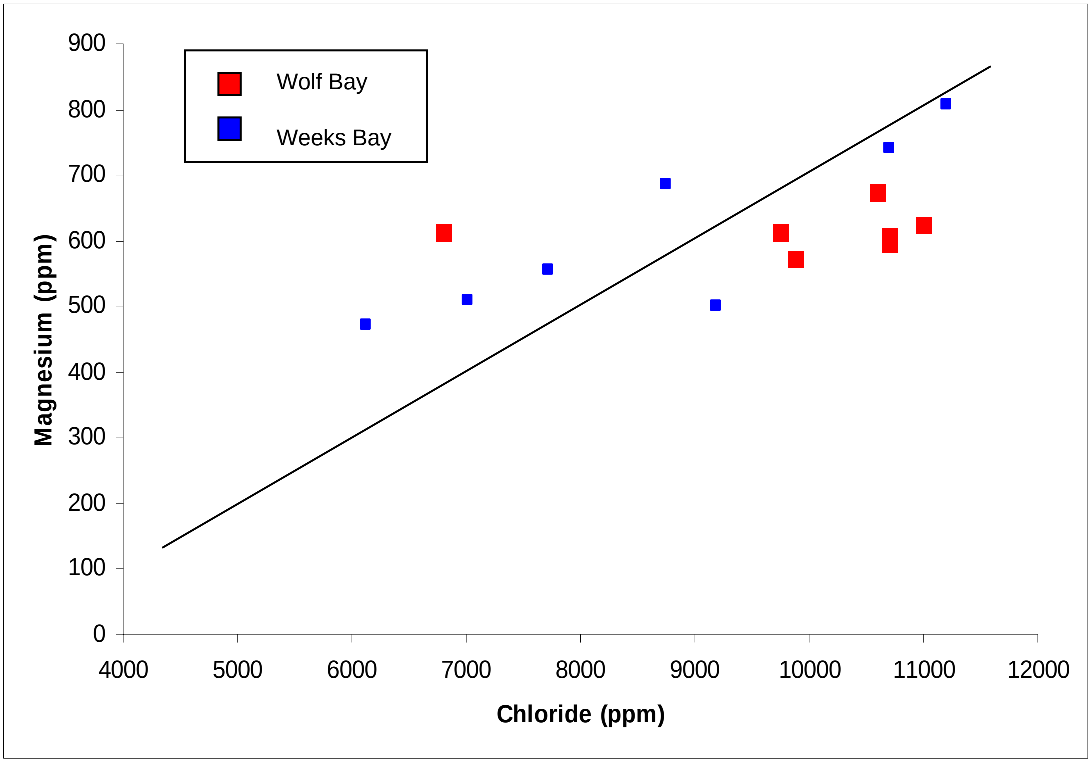


Figure 25: Plot of chloride vs. magnesium with a similar pattern between Weeks and Wolf Bay.

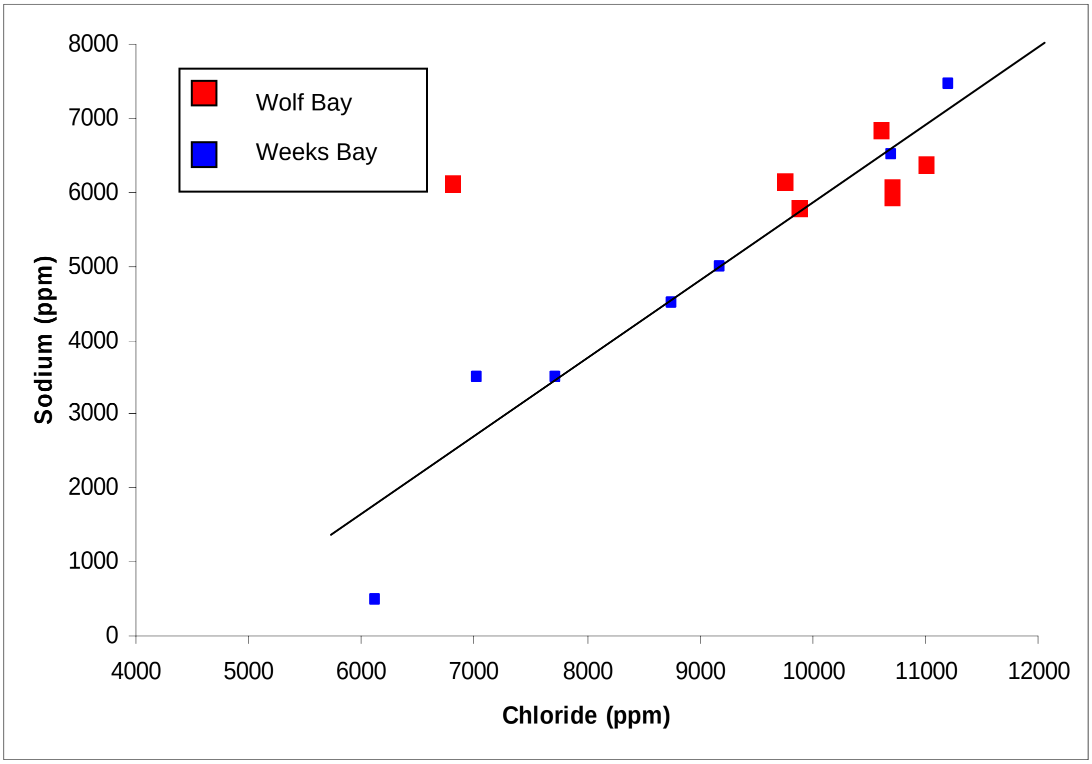


Figure 26: Plot of chloride vs. sodium showing the linear pattern of waters within Weeks Bay and the waters of Wolf Bay.

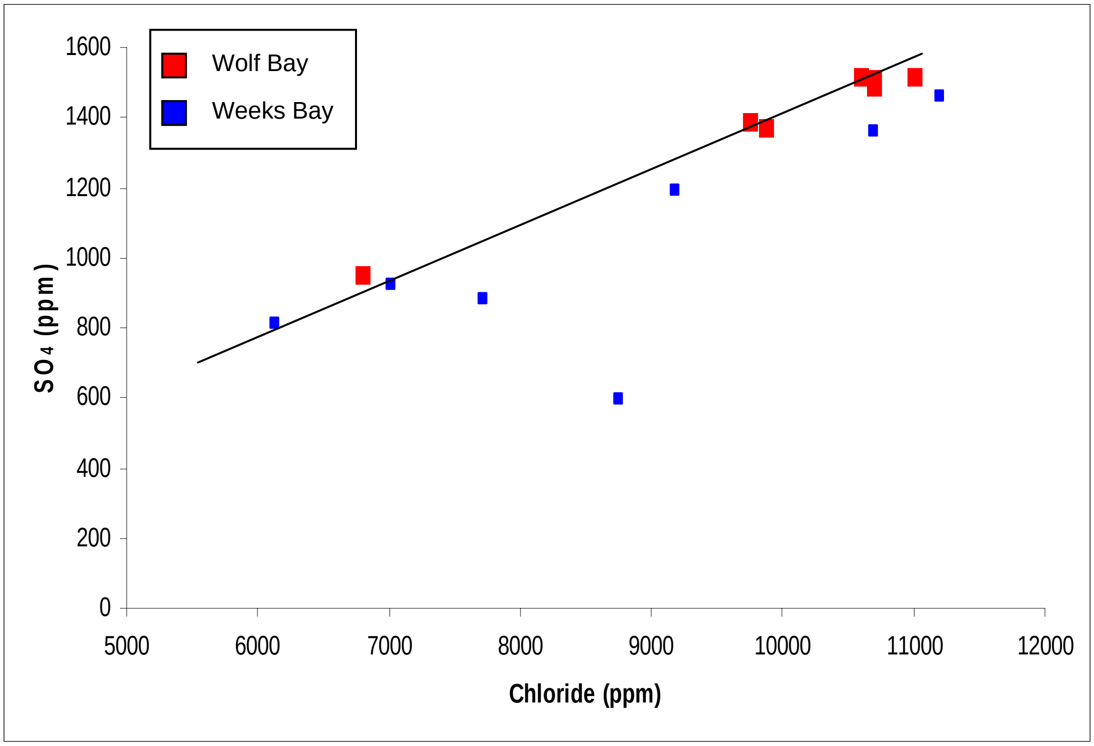


Figure 27: Plot of chloride vs. SO_4 showing the linear pattern of waters within Weeks and Wolf Bay.

Interestingly, sulfate exhibits non-conservative depletion in Weeks Bay (about 10%) and more conservative in Wolf Bay (Figure 27). Bacterial sulfate reduction in Weeks Bay may be the reason for this depletion but more microbiology research is needed to verify the biogeochemical reactions that remove sulfate.

Estuary environments show the highest levels of methylmercury in the areas near the mouths of freshwater tributaries according to previous studies. In the previous studies, the upper estuaries of freshwater/saltwater mixing zone contained low DO levels, low pH, and low salinity (Baeyens, 1998; Benoit, 1998; and Leermakers, et al., 2001). These conditions are ideal for sulfate-reducing bacteria to exist which have been shown to play a part in the methylation of mercury (Benoit 2001; King, 2002; and Monrreal, 2007). These same desired geochemical conditions may exist within Weeks Bay near the mouth of the Fish River (Monrreal, 2007), but not in Wolf Bay where water salinity is too high.

Table 10. Oxygen and hydrogen isotope composition of groundwater, bay water, and river water in Wolf and Weeks Bay watersheds.

Sample Name	**Water Source**	**$\delta^{18}O$, $^0/_{00}$ (SMOW)**	**δD, $^0/_{00}$ (SMOW)**
9	Transition Zone	-2.1	-14.9
011A	Weeks Bay	-1.2	-7.5
011B	Weeks Bay	-1	-9.6
14	Weeks Bay	-1.5	-10.1
18	Fish River	-2.3	-11.9
23	Fish River	-2.2	-15.5
27	Fish River	-2.7	-16.5
28	Weeks Bay	-2.3	-15.6
33	Weeks Bay	-1.8	-9.4
38	Weeks Bay	-1.6	-8.1
41	Weeks Bay	-1.6	-6.3
41	Weeks Bay	-1.5	-4.3
WW13	Groundwater	-4.4	-23.1
WW14	Groundwater	-4.1	-26.6
WW15	Groundwater	-2.7	-17.3
WW16	Groundwater	-4.4	-26.9
WC-1	Wolf Creek	-1.7	-6.7
WC-2	Wolf Creek	-1.5	-9.7
WB10	Wolf Bay	0.3	-0.2
WB12	Wolf Bay	0.3	-0.3
WB14	Wolf Bay	-1.6	-0.3
WB16	Wolf Bay	-1.6	-0.3
WB19	Wolf Bay	-0.4	-0.4
WB21	Wolf Bay	0.8	-0.3
WB23	Wolf Bay	-1.1	-0.4
WB26	Wolf Bay	1.8	-0.4
WB28	Wolf Bay	-0.5	-0.6
WB30	Transition Zone	-0.6	-0.5
WB31	Transition Zone	-0.9	-0.5
Sea Water		0	0

Stable Isotope Signatures of Stream Water, Bay Water, and Groundwater

Stable isotope analyses provides more details about the mixing of waters and demonstrates the role that water mixing (i.e., with groundwater and seawater) and evaporation play in influencing the chemistry of Wolf Bay and Weeks Bay surface water. Comparing oxygen and hydrogen isotopes of surface water and groundwater sampled sites along with seawater signature as well as the local meteoric water line shows how mixing and evaporation affect water chemistry in both bays (Figure 28). Deuterium (δD) and oxygen ($\delta^{18}O$) isotope ratios of groundwater and surface water in Wolf and Weeks Bay are plotted along with seawater and evaporation trajectory of the local meteoric water line (LMWL). Evaporation preferentially lifts lighter ^{16}O and ^{1}H isotopes from water to atmosphere. As evaporation occurs in surface waters, the remaining waters become enriched in heavy isotopic (^{18}O and ^{2}H) composition. Seawater is enriched with ^{18}O and ^{16}O with respect to surface meteoric water. Stable isotope signatures of groundwater fall close to the local meteoric water line, indicating very little to no evaporation or mixing prior to infiltration from pore water in the unsaturated zone. In contrast, stable isotope profiles of river water show enrichment of ^{18}O and ^{2}H, indicating they undergo greater evaporation than groundwater. The Weeks Bay water represents a mixture of three “end-member” waters: one of seawater, one of river water, and one of groundwater impacted by variations in evaporation rates. Wolf Bay water plots closer to the seawater which represents greater evaporation rates and/or more influence of seawater from the Gulf of Mexico. Isotopic signatures of Wolf Bay water also indicate less input from surface (meteoric) with respect to Weeks Bay, which is consistent with its high electrical conductivity and salinity nature. The nature and extent of hydrologic mixing and evaporation strongly influence water quality in both bays, which has profound impacts on the potential of Hg methylation in bays.

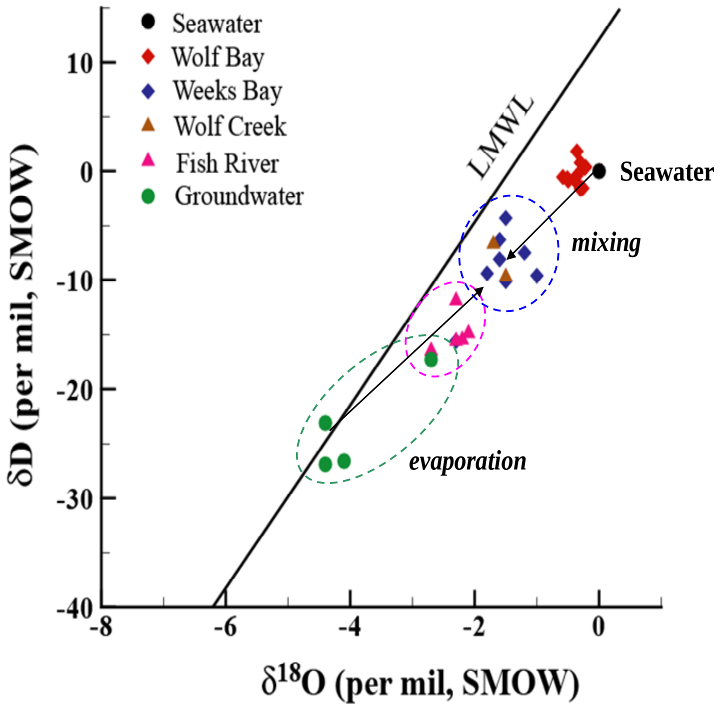


Figure 28: Plot of evaporation trajectory of local meteoric water line (LMWL) and seawater mixing trend, shown using deuterium (δD) and oxygen (δ^{18}O) isotope ratios of groundwater and surface water in Wolf Bay. The Weeks Bay water represents a mixture of three "end-member" waters: one of seawater, one of river water, and one of groundwater impacted by variations in evaporation rates. Wolf Bay water plots closer to the seawater which represents greater evaporation rates and/or more influence from the Gulf of Mexico.

SUBSURFACE GEOPHYSICAL SURVEY

Electrical Resistivity

Electrical resistivity surveys were performed on Dauphin Island at the Isle Dauphin golf course (Figure 29) and at Gulf State Park, located near Orange Beach (Figure 30). A 48-channel AGI SuperSting® Automated Resistivity Meter was used for these surveys. A 2-D dipole-dipole array was used, with an electrode spacing of three meters along the survey transect. A roll-along technique was used to extend each transect to 450 meters at Dauphin Island and 450 meters at Gulf State Park. The transects were geo-referenced using a sub-meter accuracy *Trimble* GPS.

Field data were processed using the *EarthImager2D* resistivity processing software. Results were interpreted to estimate the depth to the saltwater interface or areas of saltwater intrusion. The measured apparent resistivity, calculated apparent resistivity, and the calculated true resistivity along the transect are shown in Figure 31 for Dauphin Island and Figure 32 for Orange Beach.

Resistivity of water may vary from 0.2 to over 1000 Ω m depending on its ionic concentration and the amount of dissolved solids, and average seawater has a resistivity of 0.2 Ω m (Nowroozi et al., 1999). Resistivity of natural water and sediments without clay may vary from 1 to 100 Ω m while the resistivity of a layer saturated by saline water and some dissolved solids is in the range of 8 to 50 Ω m (De

Breuk and De Moor, 1969, Sabet, 1975, Goodell, 1986, Flanzenbaum, 1986, Zohdy et al., 1993, Nowroozi et al., 1999).

In the Dauphin Island profile (Figure 31) resistivity ranged from 0 to over 6000 Ω m. In the shallow subsurface the data yielded a wide range of resistivity readings. The higher readings probably reflect unsaturated unconsolidated sediments. The lower readings, especially in the 6-to 20-meter depth range, may indicate possible saltwater encroachment (indicated by arrows in Figure 31). These anomalies of low resistance may be the result of possible saltwater contamination within the shallow groundwater that percolated from the surface after the hurricane Katrina storm surge. The true freshwater-saltwater interface was not located. In order to detect the interface using this method, a longer transect will need to be performed to achieve a greater depth in the survey. These results imply that the depth of the saltwater wedge is greater than 50 meters.

In the Orange Beach profile (Figure 32) resistivity ranged from 223 to 4444 Ω m. These readings appear to indicate the high resistance of unsaturated layers. The survey was conducted on a golf course with multiple groundwater wells that provide irrigation to the course and it was also conducted during a drought. With the groundwater withdrawal from the wells and little to no recharge, groundwater may have been at a greater depth. The depth of the freshwater-saltwater interface was greater than anticipated therefore further studies should be conducted employing a longer transect in order to increase the depth of coverage and possible detection of the freshwater-saltwater interface.

Figure 29: Location of geophysical survey at Dauphin Island, Alabama.

Figure 30: Location map of geophysical survey at Orange Beach, Alabama.

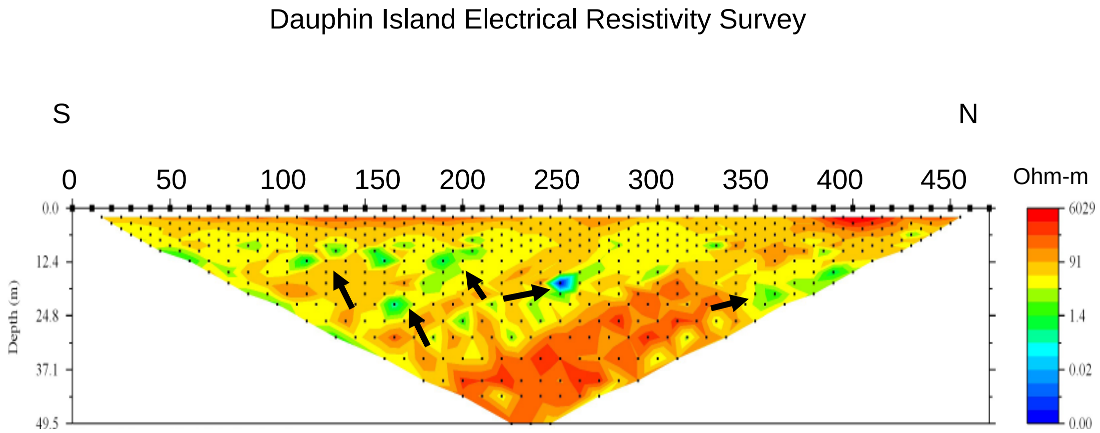


Figure 31: Results from electrical resistivity survey at Dauphin Island. The transect used an electrode spacing of 3 meters. Arrows are pointing to the low resistive anomalies in the survey. The error limit of the data was 2.72 %, which is in the acceptable range as stated in Advanced Geosciences Inc. (2002). The true resistivity was calculated using *EarthImager 2D*. (Profile location is located in Figure 29).

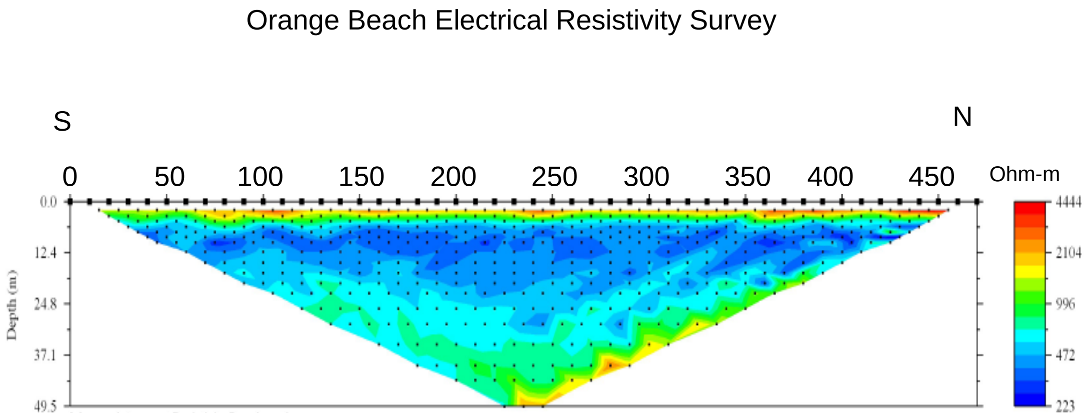
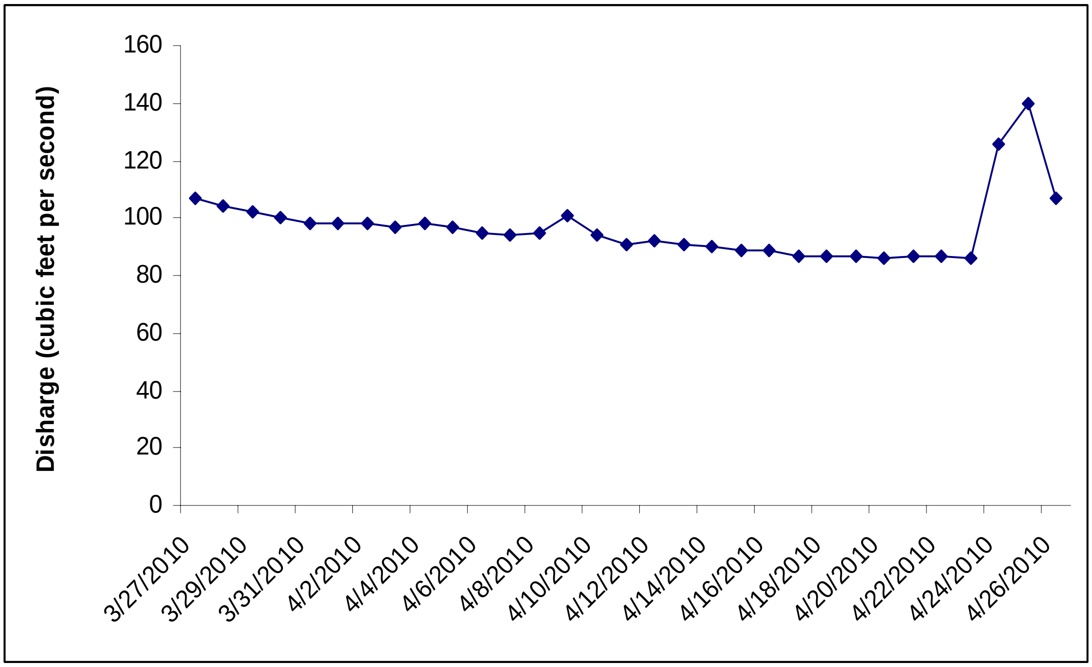


Figure 32: Results from electrical resistivity survey at Orange Beach. The transect used an electrode spacing of 3 meters. The error limit of the data was 2.74 %, which is in the acceptable range as stated in Advanced Geosciences Inc. (2002). The true resistivity was calculated using *EarthImager 2D*. (Profile location is located in Figure 30).

HYDROLOGIC MODELS

Surface Flow of Wolf Creek and Fish River

To understand and compare the influx of freshwater into Wolf Bay and Weeks Bay, data collected by the United States Geological Survey (U.S.G.S.) was obtained to compare the surface water flow into the bays (Figure 33). The USGS WaterWatch website (http://waterwatch.usgs.gov/) provides real-time, short-term (hourly) changes in gaged rivers and streams. Figure 33 shows stream discharge (ft^3/sec) computed at two USGS gage stations in 2010 at Wolf Creek (station ID 02378170), a major tributary stream of Wolf Bay, and Fish River (station ID 02378500), a major tributary of Weeks Bay. The computed USGS data show that stream discharges are much higher (~100 ft^3/sec) in Fish River than those of Wolf Creek (around 10 ft^3/sec). The high freshwater inflow allows a low-salinity water body to lie on the top of the invading salinity seawater to form a wedge interface (Figure 15). The mixing of warm, acidic, and low-salinity waters in the upper Weeks Bay (near the mouth of the Fish River) may provide favorable conditions for Hg methylation, as observed in the field. In Wolf Bay, by contrast, less freshwater inflow results in high-salinity of water throughout the bay, which in turns prevents key microbial processes that initialize Hg methylation and bioaccumulation. The result suggests that Hg biotransformation is strongly influenced by hydrochemical conditions (i.e., mixing of freshwater and saltwater) in coastal watersheds.



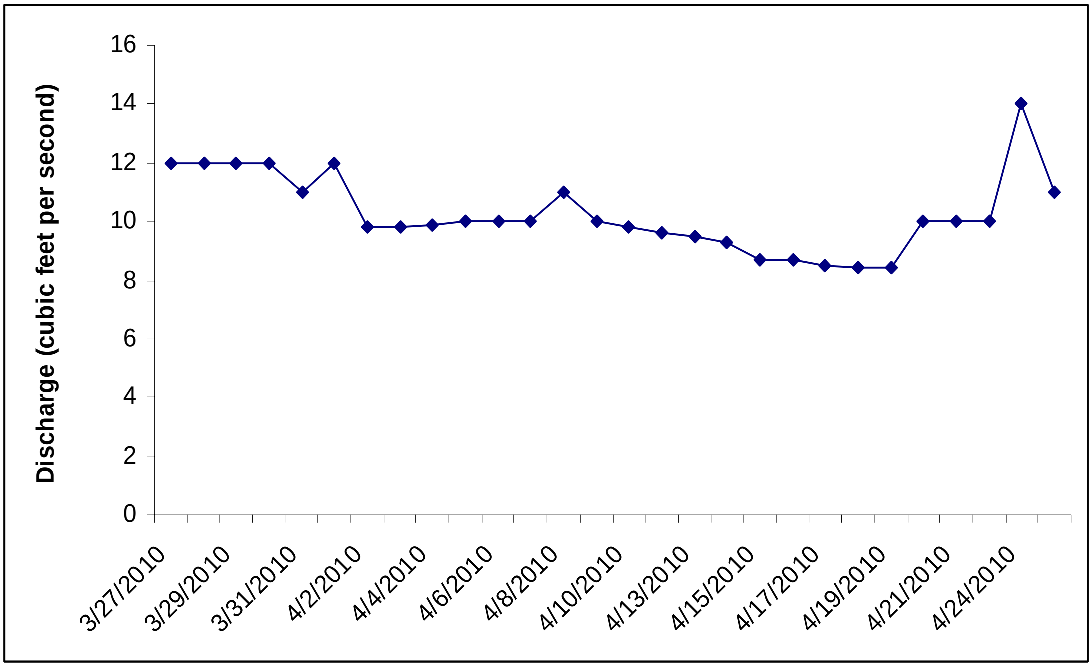


Figure 33: Hydrographs of Fish River (top) and Wolf Creek (bottom) showing discharge in cubic feet per second. (Data collected by U.S.G.S.)

Regional Groundwater Flow and Groundwater Residence Time

Figure 34 shows the measured water table elevations (Chandler, 1985) and simulated groundwater flow patterns in southern Baldwin County. Groundwater flow directions were drawn using SURFER software. Groundwater recharges at high elevations in the northern part of the study area near Loxley and migrates in the general direction of south toward the coastal areas. Moderate hydraulic gradients (on the order of a few m/km) exist in shallow aquifers in the study area. Although hydrologic properties (e.g., permeability) of the aquifers remain poorly unknown, available groundwater radioactive isotope data suggest moderate groundwater discharge rates of a few meters per year (see section below).

A regional basin hydrology program *Basin2* was used to simulate groundwater flow direction and also to calculate groundwater residence time by using the transport and decay of ^{36}Cl through the aquifers. The program uses a finite-difference grid which consists of nodal blocks that are arranged into columns and rows and cover a two-dimensional basin cross-sectional area. Each nodal point contains the properties of each block. *Basin2* calculates a number of variables such as temperature, pressure, solute (Cl) concentration, and isotopic compositions at each nodal point. The software is able to model the hydraulic characteristics and isotope transport capability of the aquifers.

Basin2 requires the construction of a cross-section that represents the stratigraphy and lithology of the basin in order to simulate groundwater flow. The data for the cross-section was entered in *Basin2* in a column format which consisted of thickness and lithologic composition (see attached CD). Thickness and composition of each unit was collected from previous stratigraphic data (Mooty, 1988). *Basin2* uses three default lithologies (sandstone, shale, and carbonate) that can be entered into the model.

Groundwater flow and residence time in Baldwin County was modeled in two-dimension using a basin-scale groundwater flow model *Basin2*. The *Basin2* model calculates groundwater flow resulting from density variation, sediment compaction, topographic relief, and the transport of heat in the basin strata. The simulation considers the regional flow in response to topographic relief and water table variations cross southern Baldwin County from Bay Minette to Orange Beach. Subsurface data from Chandler et al. (1985) were used to reconstruct the hydrostratigraphy in the cross section (Figure 35).

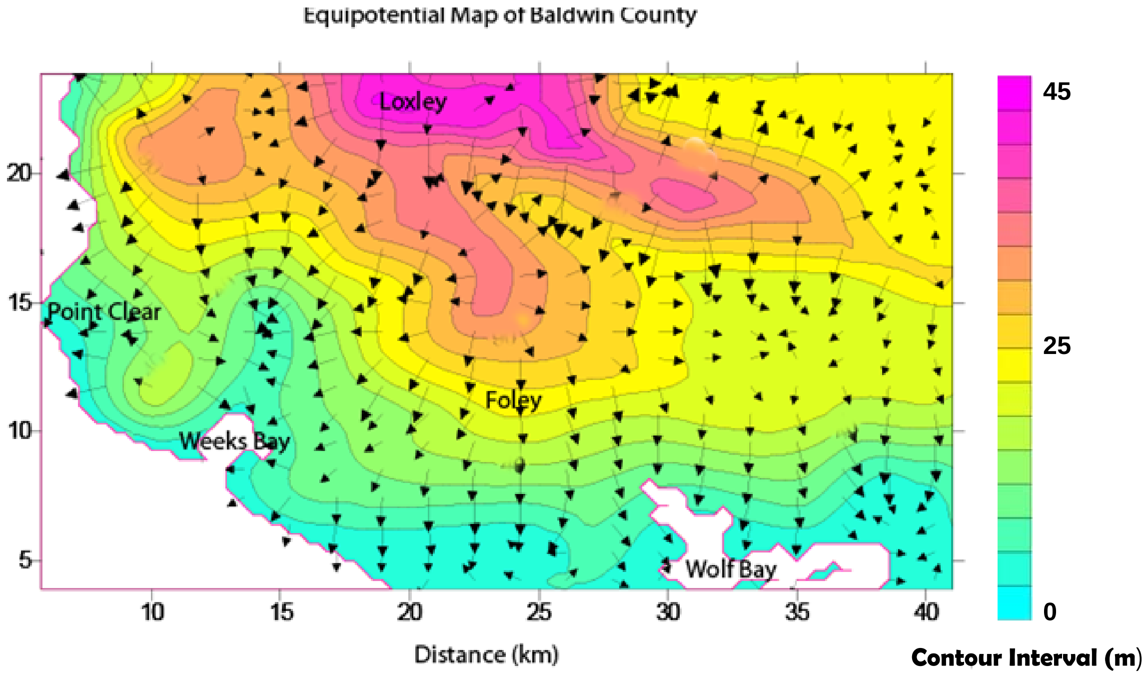


Figure 34: Equipotential map of southern Baldwin County, Alabama. Groundwater flows to the south towards the Gulf of Mexico. Also, notice how groundwater is flowing into Weeks and Wolf Bay.

The hydrostratigraphy units used in the model include sand, clay, and carbonate. Permeability of sand, clay, and carbonate are set to 10, 10^{-4}, and 10^{-2} darcy, respectively. The permeability of the sandy aquifers (Aquifer zones A1, A2, and A3) is adjusted to reflect the transport characteristics of these aquifers and the short groundwater residence time (Figure 35). The variations (and uncertainty) on permeability of clay and carbonate have little effects on groundwater flow in sandy aquifers. The sides of the basin remain open to groundwater flow. The bottom of the cross-section is set to be a no-flow boundary to reflect the low-permeability pre-Oligocene basement rocks. The input file for simulation is shown in Appendix A.

Simulation shows that groundwater migrates in the general direction to the south towards the Gulf of Mexico in all three major aquifer zones (Figure 35). The model also predicts that local groundwater flow system may exist in the shallow aquifer (i.e., Aquifer A2) where pronounced local topographic relief exists and causes undulations in the water table. Such local and shallow groundwater flow system has recharge areas near a local topographic high spot and a discharge area at the adjacent topographic low. The model predicted flow velocities are on the order of a few to tens of meters per year. The extension of the local flow system is limited to shallow depths (on the order of a few hundreds of meters) and the deeper A3 aquifer is dominated by regional flow system with more consistent north-to-south flow directions. It is expected that groundwater residence time of deeper regional flow is much longer than those of shallow local flow systems.

In Aquifer A1, the velocity arrows show that the groundwater is discharging to the surface, near the shore of the Gulf of Mexico. Groundwater in the Aquifer A2 flows to the south and then flow upwards into the A1 aquifer around the discharge area. Groundwater flow in the aquifer seems to be going either upward or downward where it encounters the clay unit.

The A3 aquifer, the largest of the three aquifers, is dominated by a regional flow that is directly south and appears to discharge into the Gulf of Mexico. The Pensacola Clay which is located at the southern end of the base of the study area has an upward flow where it is narrowly overlying the carbonate sequence and a more southerly flow through the thicker part of the unit. The northern part of the study area at the base lies the carbonate unit which pinches out in the Pensacola Clay. The flow through the carbonate has a direct southern flow.

The flow is driven by hydraulic gradients caused by topography and discharges into the Gulf of Mexico. The A2 aquifer is an active flow system that has a calculated recharge rate of 40+/-16 cm/yr (from Dowling et al., 2004). The A3 aquifer has a calculated horizontal velocity of 13+/-5 m/yr which suggests that substantial ground water discharge to the ocean is occurring in this aquifer. The flow rates with ^{14}C and ^{4}He groundwater ages (or residence time) of 375-7500 years (i.e., the time since recharge) along flow path of 30 to 70 km were calculated by Carey et al. (2004).

Comparing the models produced by *Basin2* to previous studies conducted in the A3 aquifer, it seems that the calculated residence time is comparable to the isotope ages suggested by Dowling et al. (2004) and Carey et al. (2004). Carey and others (2004) (Figure 36) estimated that the groundwater ages range from 730 years near the top of the aquifer, below the aquitard, to 6630 years found in the deeper A3 aquifer near the coast above the seawater encroachment line. The average age of waters sampled and analyzed in Carey's model is 3033 years. As expected the deeper units have the oldest groundwater and the recharge area at the northern end of the model of all aquifers have younger waters in the *Basin2* model (Figure 37). According to Carey et al. (2004), high ^{14}C level near the recharge area represents the youngest groundwater with strong atmospheric signature; groundwater ages as it migrates away from the recharge area (Figure 38). The ages of water in the *Basin2* model appear to be in the less than 3000 - 6000 years range, with the older waters discharging into the Gulf of Mexico and younger waters closer to the recharge areas.

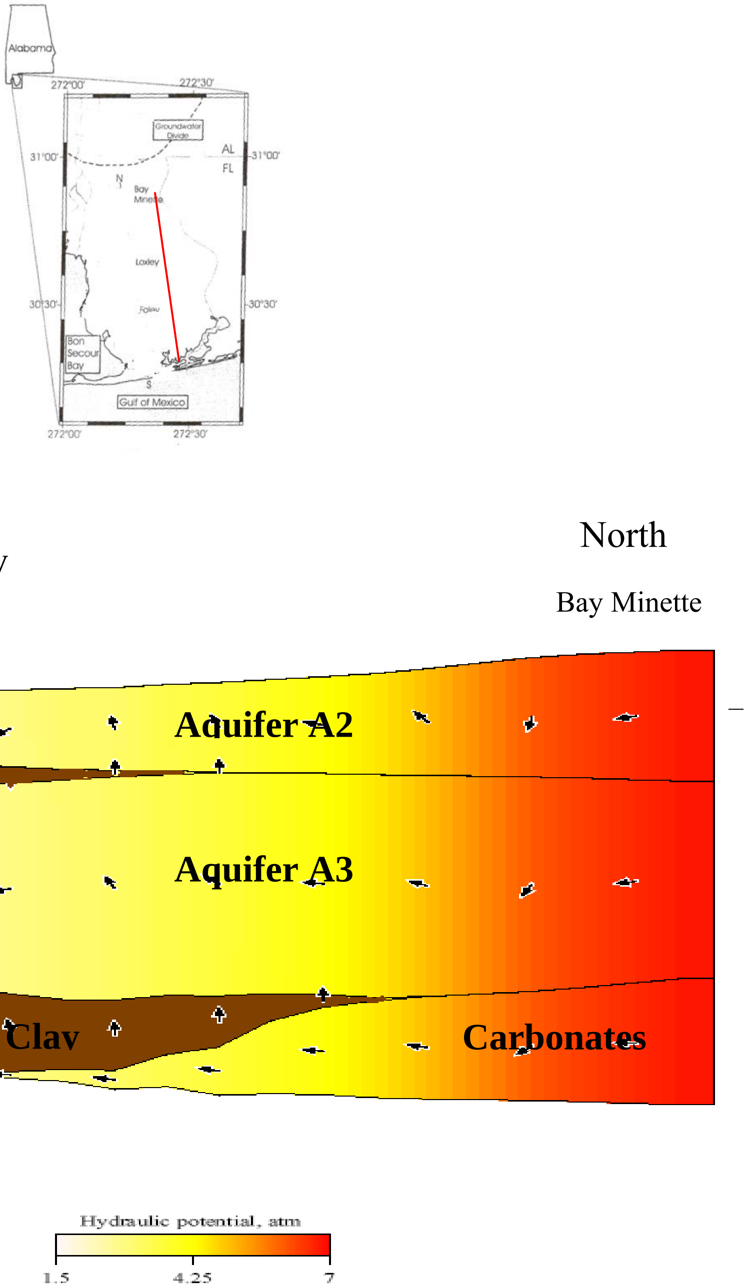


Figure 35: Calculated regional groundwater flow from north to south in Baldwin County. Arrows indicate groundwater flow direction in the aquifers.

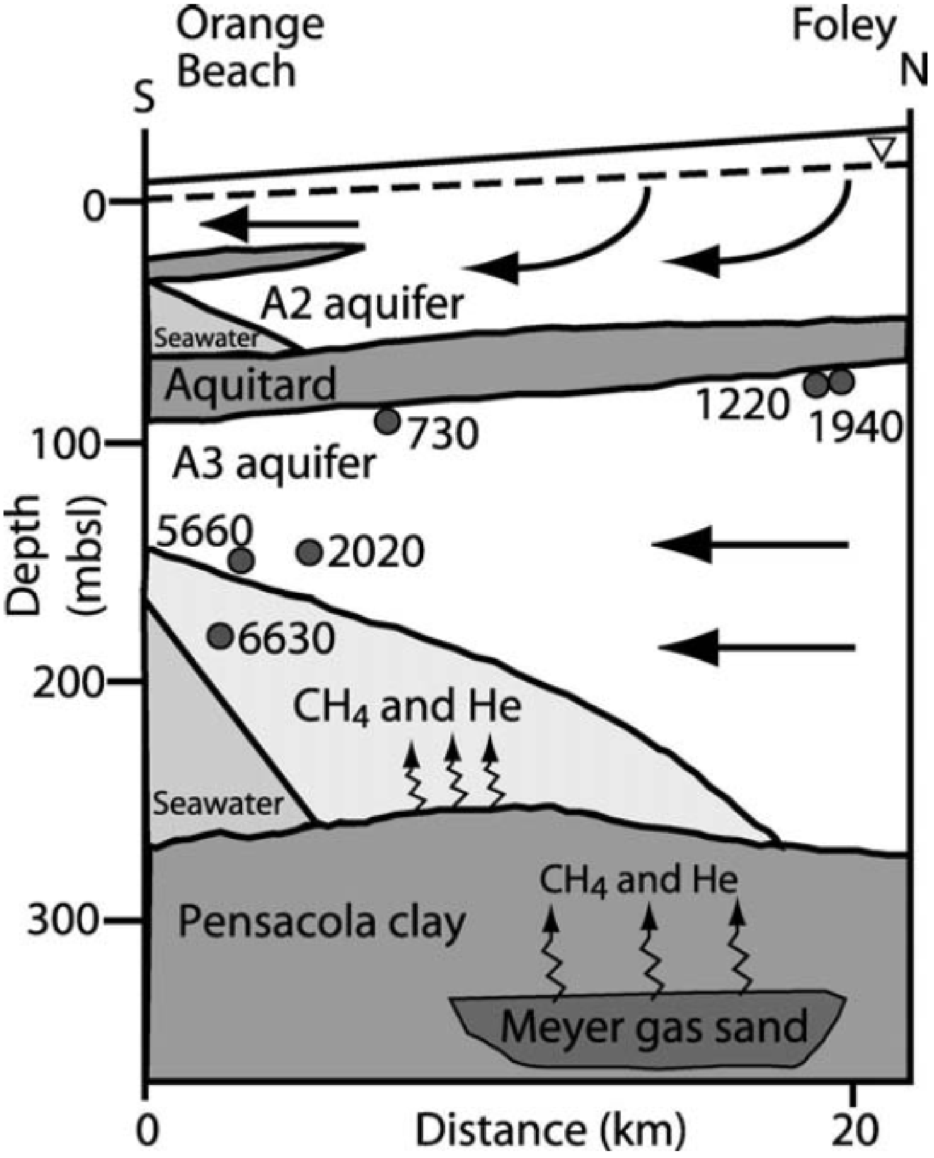


Figure 36: Cross-section of A2 and A3 aquifers in southern Baldwin County with circles representing the location and depth of samples with the corresponding ages of water from Carey et al. (2004) and Dowling et al. (2004).

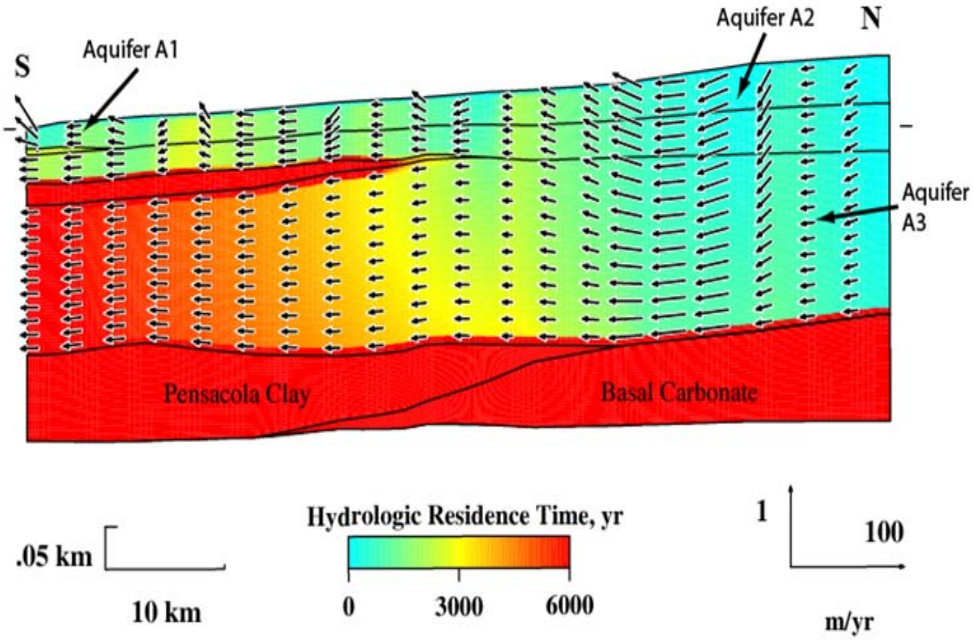


Figure 37: *Basin2* model showing calculated residence time (color map) in southern Baldwin County (see Figure 35 for plan view reference).

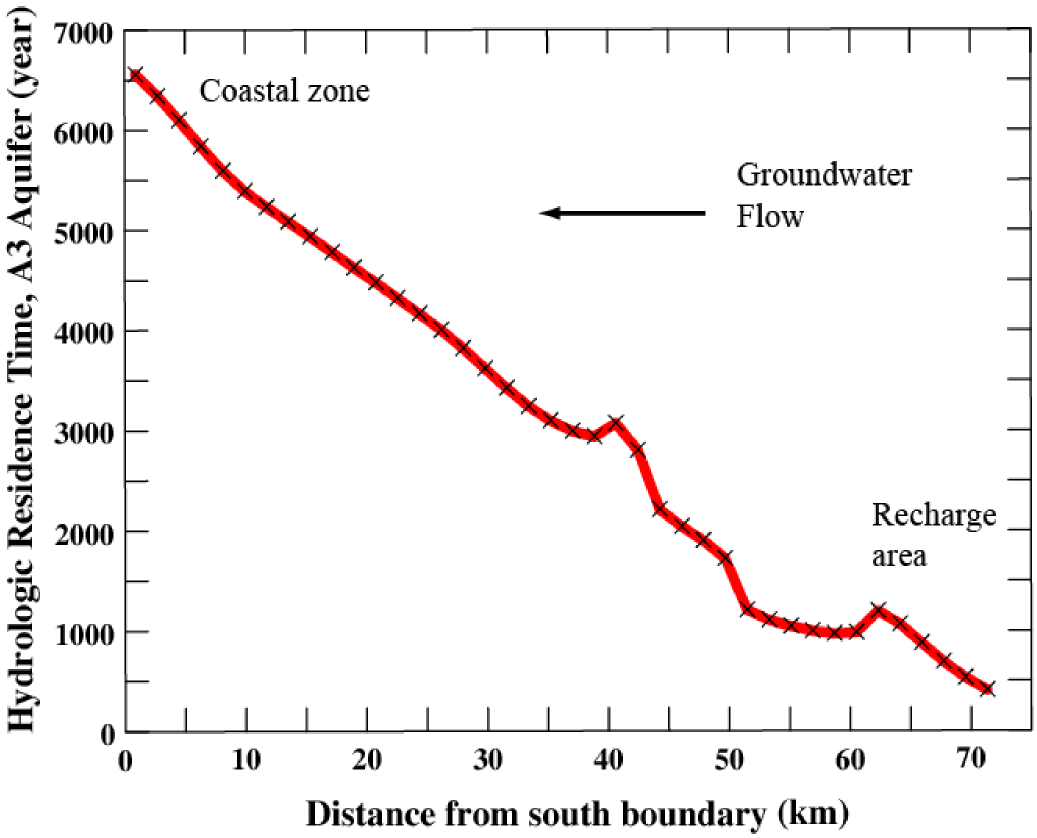


Figure 38: Plot of hydrologic residence time in the A3 aquifer vs. distance.

CONCLUSIONS

The mixing that is taking place within the Weeks Bay and Wolf Bay watersheds strongly impacts the water chemistry and also the methylation of mercury especially in Weeks Bay. The mixing of seawater, freshwater, and groundwater in Weeks Bay provides desired geochemical conditions (i.e. warm, low pH and low salinity) that are necessary for methylation. Surface water in both bays are Na-Cl type. Wolf Bay has a higher salinity (closer to seawater) that prohibits the favorable conditions to promote methylation of mercury. The oxygen and hydrogen isotope data suggest that the chemistry and quality of surface waters of river, creeks, and bays are affected by evaporation, meteoric recharge, groundwater discharge, and mixing with seawater. The stable isotope signatures of groundwater fall close to the LMWL, which indicate minimum evaporation prior to surface discharge. Fish River water and Weeks Bay water show enrichment of ^{18}O and ^{2}H relative to groundwater, indicating that they undergo greater evaporation or mixing with isotopically heavier seawater. Wolf Bay water is enriched in heavy ^{18}O and ^{2}H with respect to those in Weeks Bay, this and its higher salinity reflects less freshwater inputs and greater proportion of seawater mixed in the bay. Geochemical analysis suggests that, most major ions (Na^{+}, Ca^{2+}, Mg^{2+}, Br^{-}, etc.), with the exception of SO_4^{-2}, exhibit conservative behavior during water mixing in Weeks Bay but most exhibit a more non-conservative behavior in Wolf Bay. Along with physical mixing and evaporation, biochemical processes such as sulfate reduction due to bacteria may be at work in the Weeks Bay watershed as indicated by non-conservative depletion of

SO_4^{-2}. It is known that bacterial sulfate reduction is the critical first step for Hg methylation and bioaccumulation.

The intrusion of seawater into Wolf Bay and Weeks Bay creates a front of high salinity, high pH water that penetrates below low pH, low-conductivity freshwater. Along this wedge interface, water at different depths exhibit difference in water chemistry. The higher discharge of low pH, low-salinity surface water (i.e., Fish River) into Weeks Bay may contribute vital conditions that promote the methylation of mercury. By contrast, salinity in Wolf Bay may be too high for the methylation to take place. The most rapid changes in water chemistry occur at the mouth of Wolf Creek flowing into Wolf Bay and in Weeks Bay at the mouth of the Fish River. The mixing of several waters of different chemical characteristics creates a favorable environment (i.e., the presence of higher temperature, low pH, and low-salinity waters) where methylation may occur and cause the spread of mercury contamination throughout the watershed via bioaccumulation in Weeks Bay but not Wolf Bay. Low DO and ORP values observed in this mixing zone suggest active microbial processes that are an important factor in initializing Hg methylation in Weeks Bay near the mouth of the Fish River, but Wolf Bay has higher DO values in this mixing zone. Our results imply that Hg biotransformation is strongly influenced by hydrochemical conditions in coastal watersheds.

The most likely source for mercury contamination found in the southern Baldwin County watersheds is from atmospheric deposition. By examining the precipitation data from the USGS and mercury deposition data from the MDN show that an increase in precipitation results in an increase mercury deposition in the watersheds.

The geophysical surveys conducted on Dauphin Island and Orange Beach yielded mixed results. On Dauphin Island the electrical resistivity survey had readings that ranged from highly resistive (unsaturated layers) to low resistive, which possibly indicating saltwater in the shallow subsurface. The results from the survey conducted in Orange Beach indicated that the shallow subsurface is comprised of highly resistant unsaturated layers and not likely to be contaminated by shallow saltwater. The freshwater-saltwater interface in this area turned out to be deeper than anticpated. A longer survey length would be needed in order to locate the depth of the freshwater-saltwater interface.

Regional scale groundwater flow models were developed in a cross section extending from the northern recharge areas (near Bay Minette) to the Gulf Coast. The model predicted two flow regimes in major aquifer zones. A local flow regime is present in Aquifer A2 due to local variations in topography and water table undulations. In the deeper Aquifer A3, a regional flow regime dominates in which flow directions are more consistent (i.e., from north to south) and controlled by the net topographic slope. Groundwater discharges southwards into the coastal estuaries (e.g., Wolf and Weeks bays) and Gulf of Mexico. Calculated groundwater flow velocities in major aquifers range from a few to tens of meters per year. The model calculated that groundwater residence time of major aquifers ranges from 0 near the recharge area to about 7000 years near the Gulf Coast along a 70 km flow path. The calculated groundwater residence time is consistent with ^{14}C and ^{4}He ages measured by Carey et al. (2004).

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