HYDROLOGY AND WATER CHEMISTRY IN WEEKS BAY, ALABAMA:

IMPLICATIONS FOR MERCURY BIOACCUMULATION

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HYDROLOGY AND WATER CHEMISTRY IN WEEKS BAY, ALABAMA: IMPLICATIONS FOR MERCURY BIOACCUMULATION

Robert Horvath Monrreal

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Date of Graduation

VITA

Robert Horvath Monrreal, son of John Monrreal and Mary Horvath, was born on April 25, 1981, in Detroit, Michigan. He attended Pope Paul VI Catholic High School in Fairfax, Virginia, and graduated in the spring of 1999. After high school he attended Old Dominion University in Norfolk, Virginia, and graduated in December 2003 with a Bachelors of Science in Geology. Shortly after receiving his undergraduate degree, he started graduate school at Auburn University in the fall of 2004.

THESIS ABSTRACT

HYDROLOGY AND WATER CHEMISTRY IN WEEKS BAY, ALABAMA: IMPLICATIONS FOR MERCURY BIOACCUMULATION

Robert H. Monrreal

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Recent studies within Weeks Bay, an estuary of Mobile Bay, have revealed that both water and fish are contaminated by mercury (Hg), an element known to be extremely toxic to wildlife and humans. Seasonal variations of total mercury in precipitation were analyzed using data collected at two Mercury Deposition Network stations. The results showed that the most likely source for mercury is from atmospheric deposition. Once in an aqueous environment, inorganic mercury can methylate to toxic methylmercury (CH_3Hg). To understand the water chemistry in which mercury methylates, seasonal measurements of temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), specific conductance (SpC), and dissolved organic carbon (DOC) were conducted in water samples taken from Weeks Bay, from groundwater wells, and from a major surface tributary. Correlations of these constituents indicate that high salinity and pH seawater invade below acidic, low salinity water in the bay to form a wedge interface. The mixing of warm, acidic, and low-salinity waters in the upper bay (near the mouth of the Fish River) provide a favorable conditions for Hg methylation. Low DO and ORP values observed in this mixing zone indicate high microbial activities that may initialize Hg methylation. Geochemical analyses show that most major ions exhibit conservative behavior while sulfate shows slight depletion during water mixing. River and bay water are enriched in ^{18}O and ^{2}H relative to groundwater, indicating they have undergone greater evaporation or mixing with isotopically heavier seawater. In summary, water chemistries can vary both spatially and seasonally in the bay based on environmental conditions. Storms, stream discharge, and seasonal climate changes can affect the conditions within the bay. Seasonal data indicate that high temperature, low pH, low conductivity, low DO, conditions ideal for mercury methylation are found in the bay especially during summer months.

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INTRODUCTION

In recent years there has been an increase in the amount of mercury (Hg) found in the waters in and around the Gulf Coast region of the United States. Mercury is an element known to be extremely toxic to wildlife and humans. The amount of mercury detected in these waters exceeds the EPA drinking water standards of 2 parts per billion (ppb) and poses a threat to human health. It is from these waters that mercury can be introduced into the human body, either from drinking water contaminated by mercury or by eating fish that live in mercury contaminated waters.

Mercury contamination can result from both natural and anthropogenic sources. Mercury exists as numerous species in natural aqueous environments, some of which are more stable than others. These different species of mercury include elemental mercury (Hg), oxidized, reduced, or ionic mercury (Hg^{2+}), and methylmercury (CH_3Hg). The unstable forms of mercury are the most hazardous to human health because they are easily broken down and placed into solution. The speciation and transportation of mercury in aquatic environments are controlled mainly by the water chemistry. The common factors that determine Hg speciation include dissolved organic matter, chloride, sulfide, redox conditions, and pH (Ravichandran et al., 1998).

Mercury can be found as many types of trace constituents and its principal minerals cinnabar (HgS), corderoite ($Hg_3S_2Cl_2$), and livingstonite ($HgSb_4S_8$). Major anthropogenic sources of mercury are coal burning power plants. When burned, mercury turns into a vapor phase and is transported through the atmosphere as elemental and oxidized mercury. Elemental mercury has a residence time of up to a year in the atmosphere, whereas oxidized mercury has a residence time of only a few days. This is due to the higher solubility of Hg^{2+} in water which allows for mercury to return to the surface during rain falls. The longer the residence time, the farther mercury can be transported through the atmosphere. As a result, much of the world's mercury pollution is mainly a result of atmospheric deposition (Senior et al., 2000).

Health concerns from fish consumption have forced advisories against eating fish portions of nearly every state. The most susceptible areas to mercury contamination appear to be coastal waterways and estuaries. Of the United States coastal waters, 65 % contain advisories; this includes 100 % of the Gulf Coast and 92 % of the Atlantic Coast (EPA, 2005). Due to the contamination issues studies have been performed in some of the United States' larger bays and estuaries, these include; the San Francisco Bay Estuary, the Chesapeake Bay, and the Mobile Bay (Benoit et al., 1998; Mason et al., 1999; Lawson et al., 2001; Conaway et al., 2003; and Warner et al., 2005).

Weeks Bay is an estuary located in eastern Mobile Bay and is economically important to Alabama due to its large seafood industry (Fig. 1). In 1992 Weeks Bay designated as an "Outstanding national Water Resources" by the EPA (1999). Both the Fish and Magnolia Rivers drain into Weeks Bay before reaching Mobile Bay and eventually the Gulf of Mexico. Weeks Bay consists of 126,000 acres of watersheds with a diverse suite of depositional environments and ecosystems in Baldwin County. Several watersheds in the region are surrounded by urban centers that host large industrial and agricultural activities, all of which are potential point and non-point sources of Hg

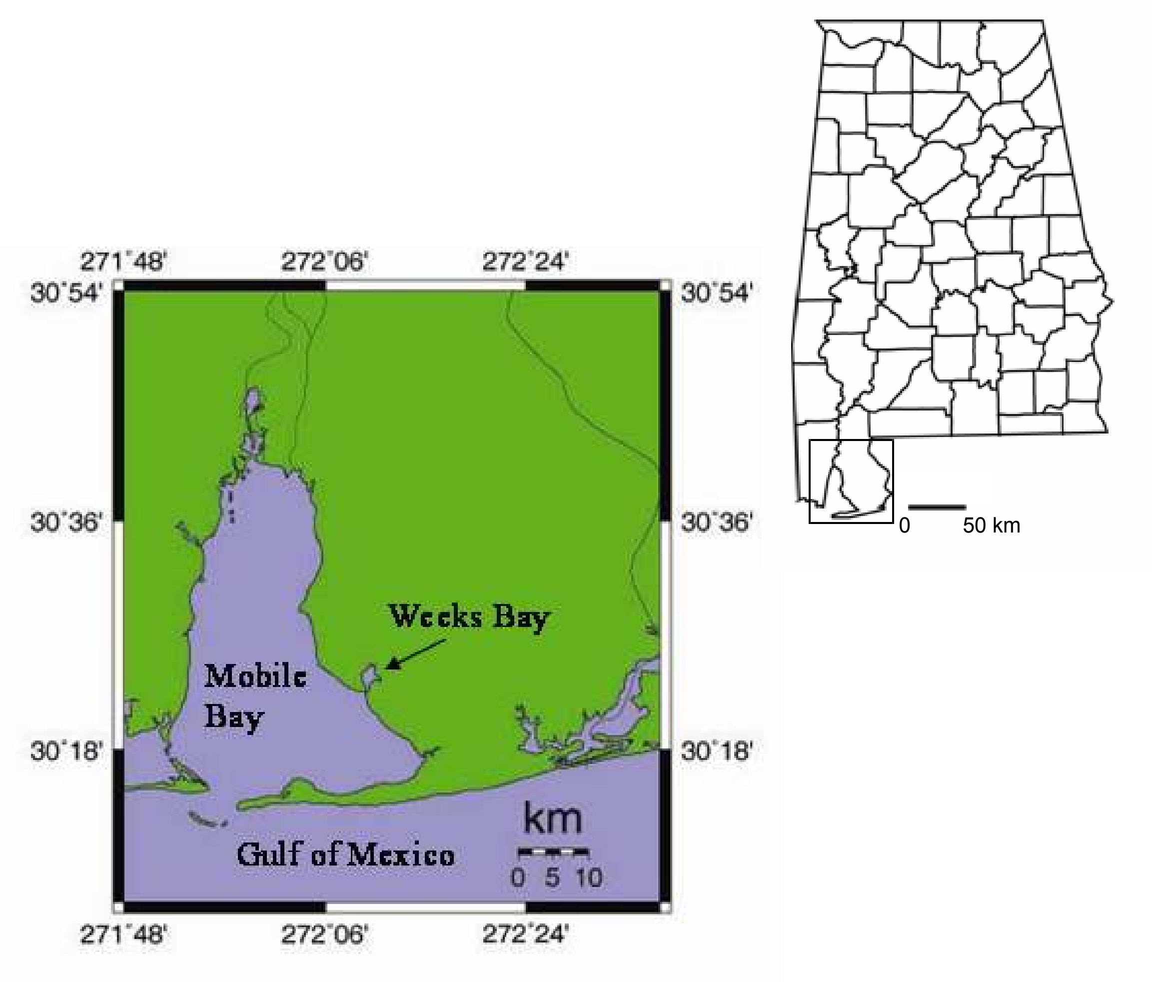

Figure 1. Weeks Bay, an estuary of Mobile Bay, is located in southwestern Alabama's Baldwin County and has a watershed of 126,000 acres. Fish, such as Largemouth Bass, caught within the Weeks Bay watershed have been found to contain mercury levels above Federal Food and Drug Administration standards of 1 mg/kg.

pollution. The ecosystems, depositional environments, and stratigraphy of Weeks Bay have been studied by various investigators (Brannon et al., 1977; Haywich et al., 1998; U.S. Fish & Wildlife Service, 1996; Fisher et al., 2006).

Largemouth Bass in Weeks Bay have been found to contain Hg greater than 1 μg/L (M. Shelton personal communication). A health standard issued by the Federal Food and Drug Administration requires that fish contain less than 1 μg/L. Despite many previous studies, the sources, sinks, and cycling of Hg and general hydrology in this estuary remain poorly understood. Estuaries and bays are believed to be the primary traps for mercury contamination due to the low percentage of mercury exported to the ocean (Mason et al., 1999, Kim et al., 2004). This study initialized field and laboratory analysis to collect general hydrology and water chemistry data of the bay. The results will assist in the understanding of how the water chemistries within Weeks Bay change throughout the year and the effects of these changes may have on the methylation of mercury.

MERCURY CONTAMINATION

Mercury Sources

Mercury can be found as trace constituents in many types of rocks within the Earth's crust. At room temperature mercury is a liquid and can be volatized at low temperatures. This allows mercury to become a vapor and can lead to worldwide contamination problems through atmospheric circulation. Mercury sources are both natural and anthropogenic. Natural occurrences of volatized mercury include volcanoes and associated geothermal systems, fires, and the evaporation of seawater. Anthropogenic sources of mercury are more common and have a relatively steady rate of expulsion since the industrial revolution.

Anthropogenic sources include numerous industrial processes and waste incineration. As coal is burned, mercury sequestered in the organic matter is volatized and released. The mercury that exists in the coal is the result of organic matter bonding with mercury from atmospheric deposition and from mercury enriched waters. As the organic matter is compacted and transformed into coal mercury levels are concentrated. (Senior et al., 2000; Yudovich and Ketris, 2005).

Mercury Speciation

Mercury exists as numerous species, some of which are more stable than others under various Eh-pH conditions (Fig. 2 and 3). All forms of mercury can create health problems in humans and have a variety of affects based on the species that is introduced into the body. Which species of mercury exists in aquatic environments is controlled by water chemistry. The common factors that determine speciation include dissolved organic matter, chloride, sulfide, and pH (Suzuki et al., 1992; Ravichandran et al., 1998). Ionic Hg is dominant under oxidizing conditions (Fig. 2). Solid elemental Hg and Hg sulfide (cinnabar) become the dominant phases under reducing conditions. In Cl-rich environments, the formation of aqueous HgCl complex could enhance the solubility and mobility of Hg (Fig. 3). Grassi and Netti (2000) showed similar results between increased Cl^- levels and an increase in the amount of mercury in solution.

Atmospheric Deposition

As mercury vapors enter the atmosphere a wide variety of processes can occur based on the forms of mercury that exist. Hg^0 and Hg^{2+} are the most common forms of mercury that exist in the atmosphere. The removal process of mercury from the atmosphere plays a major role in the contamination of waterways due to the ability of atmospheric mercury to be transported long distances. Deposition can take place in wet or dry processes. The interaction of mercury with other atmospheric gases, such as aerosols and ozone, assist in the deposition process. High levels of mercury within the atmosphere results in both wet and dry deposition, lower Hg levels rely on the oxidation

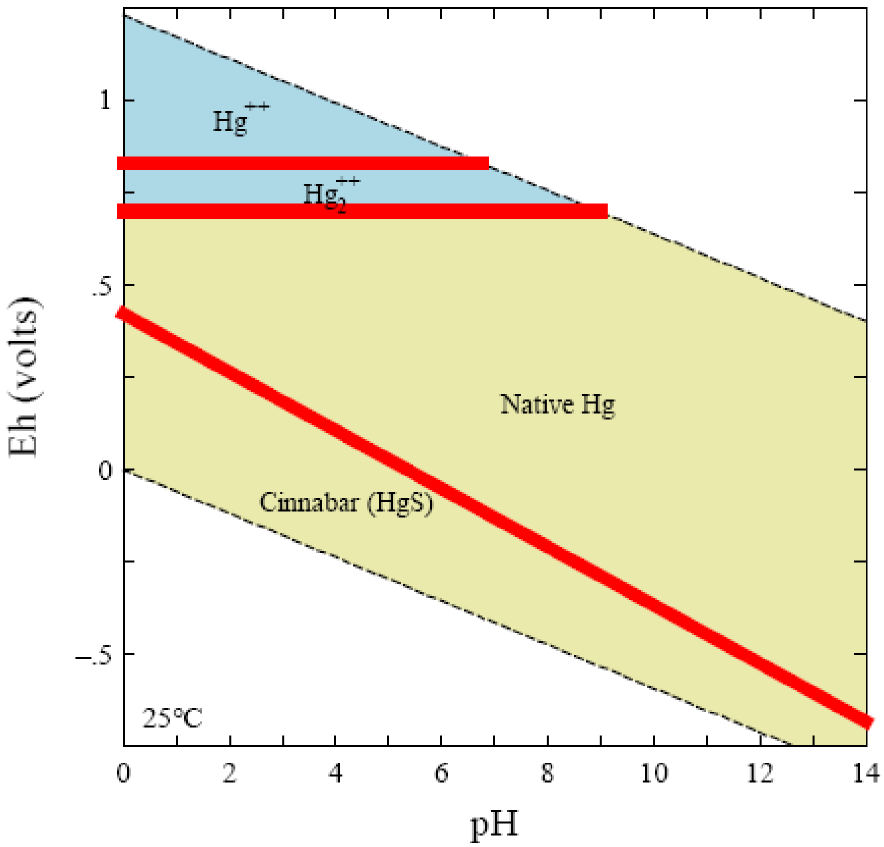

Figure 2. Eh – pH diagram drawn at 25°C for Hg-Sulfur system showing pertinent mercury species pH at $a_{Hg} = 0.001$, $a_{SO4} = 0.1$. Blue areas indicate conditions where mercury is soluble while green areas indicate conditions in which mercury exists in a solid state. The diagram was constructed using the Geochemist's Workbench (Bethke, 1996).

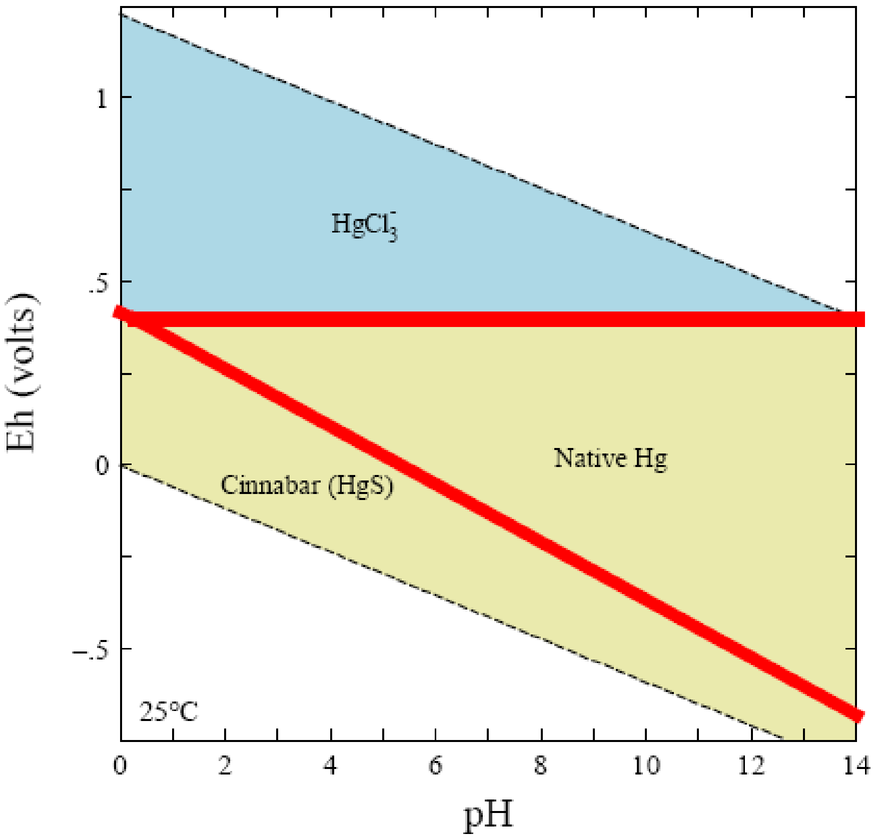

Figure 3. Eh – pH diagram drawn at 25°C for Hg-Sulfur-Chlorine system showing pertinent mercury species pH at $a_{Hg} = 0.001$, $a_{SO4} = 0.1$, $a_{Cl^-} = 0.1$. The addition of chlorine increases the solubility of mercury. This diagram was constructed using the Geochemist's Workbench (Bethke, 1996).

of Hg^0 to allow mercury to bond with other atmospheric gases resulting in deposition. An additional process that may result in dry deposition is the formation of mercuric oxide (HgO), a solid particulate, which may return to the surface under dry conditions (Schroeder and Munthe 1997).

The amount of mercury contamination resulting from atmospheric deposition is monitored by the National Atmospheric Deposition Program (NADP). A special series of sites have been devoted to collecting wet atmospheric mercury deposition data as part of the Mercury Deposition Network (MDN). Throughout the United States there are 88 MDN mercury monitoring sites that monitor Hg concentrations (µg/L) and total Hg wet deposition ($\mu g/m^2$). These sites collect precipitation, which is then sent to analytical laboratories for total concentration analyses.

Mercury Methylation

The methylation of mercury to create methylmercury (CH_3Hg) is a process that takes place in aqueous environments under favorable geochemical conditions. Recent research suggests that methylation can occur in both the water column and in sediments (Sunderland et al., 2004; 2006; Warner et al., 2005). In aqueous environments, methylation ideally occurs in conditions of low pH, low dissolved organic content (DOC), low salinity, and low oxidation-reduction potential (ORP), with high temperature and sulfate content (Suzuki et al., 1992; Celo et al., 2005; and Mason et al., 2006). Many of these factors do not exist at the requisite levels for methylation in seawater. Mixing of freshwater with seawater provides more favorable geochemical conditions.

The aqueous geochemistry conditions involved with methylation are closely related to each other and can have a wide range of effects based on various factors. DOC, pH, and ORP help create conditions that assist in microbial activity. High DOC values have been shown to hinder the methylation process; however, DOC provides electron donors for bacteria, such as sulfate-reducing bacteria (SRB). Low ORP values are a result anaerobic conditions caused by increased microbial activity Finally, low pH allows heavy metals to be released and become available for chemical reactions (Baeyens et al.; 1998, Mehrotra, et al., 2003) .

High temperatures appear to assist in the methylation process as evidenced by increased methylation during the summer months, when waters are warmer. Generally, seawater in the region is warmer than freshwater and may provide higher temperatures for methylation. However, the increase of salinity due to the addition of seawater hinders methylation process due to increased sulfides that may take in Hg to form insoluble HgS (Compeau and Bartha, 1986). It is likely that maximum methylation may occur in the freshwater-seawater mixing zone.

Climate also plays a vital role in mercury methylation in estuarine environments, where methylation commonly takes place. Factors such as rainfall and wind can hinder or assist in the methylation process. Substantial rainfall events can affect the water chemistry of aqueous environments and may add nutrients and additional heavy metals from erosion or surrounding terrain. Wind can also play a part in methylation. Little to no wind can result in thermal and haline stratification of water bodies, effecting methylation. On the other hand, strong sustained winds can cause mixing of shallow waters which may bring low oxygen waters to the surface and affect water column biota (Mason et al., 1999).

Biomagnification and Bioaccumulation

The health concerns involved with mercury are mainly the result of the ingested of mercury contaminated organisms. The methylation process converts mercury to CH_3Hg, a form that can be consumed by various organisms and enter the food chain. Plankton and other bacteria consume methylmercury becoming contaminated. As predators feed on mercury contaminated lower organisms, concentrations of mercury within the food chain increase (Lawson and Mason, 1998). This results in the top predators, such as eagles and humans, ingesting the highest levels on mercury creating increased health concerns.

Weeks Bay Geology

Weeks Bay is located in Baldwin County, Alabama on the Gulf Coast coastal plain. Gulf Coast deposits typically consist of mostly sands and gravel deposits with some interbedded silts and clays. The coastal plain sediments can be divided into three major deposits that are considered as local aquifers. Sediments of the Miocene age are composed of white- to light-grey, fine to very coarse sands with some interbedded sandy, silty clay. Pleistocene deposits are similar to those of the Miocene but have greater abundance of interbedded sandy, silty clays. 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).

Hydrologic Effects on Mercury Cycling

Groundwater discharge and surface evaporation can also affect the chemistry and salinity of surface water, which in turn control the biotransformation of Hg in aqueous environments. Groundwater discharge can be analyzed by measuring hydraulic heads of clustered wells at different depths. The evaporation and geochemical evolution of surface water and groundwater can be traced by stable isotope (^{18}O and ^{2}H) analyses.

METHODOLOGY

Field, laboratory, and computer analyses were conducted to study the source of Hg and how near-surface processes such as water mixing and evaporation could potentially affect the biogeochemical cycle of Hg in Weeks Bay. Weekly concentrations of total Hg in precipitation were collected from the Mercury Deposition Network (MDN) for a period of one year to gain information on seasonal trends in Hg deposition from atmospheric sources.

To study the hydrology effects of water mixing and evaporation within the bay, water samples were collected from nearby groundwater wells, surrounding rivers, and from the bay for major ion, trace element, and stable isotope analyses. The data were then compiled and analyzed using a variety of computer and mapping programs to understand better water mixing within the bay and how it affects mercury methylation. Four trips were taken to the Weeks Bay area to collect data and water samples for chemical analyses. These trips were taken over the course of a year so that seasonal variations of hydrology and water chemistry within the bay could be determined.

Mercury Deposition Analysis

Mercury deposition data were compiled from two MDN sites, AL02 and AL24 (http://nadp.sws.uiuc.edu/mdn/) in and around the Weeks Bay watershed (Fig. 4).

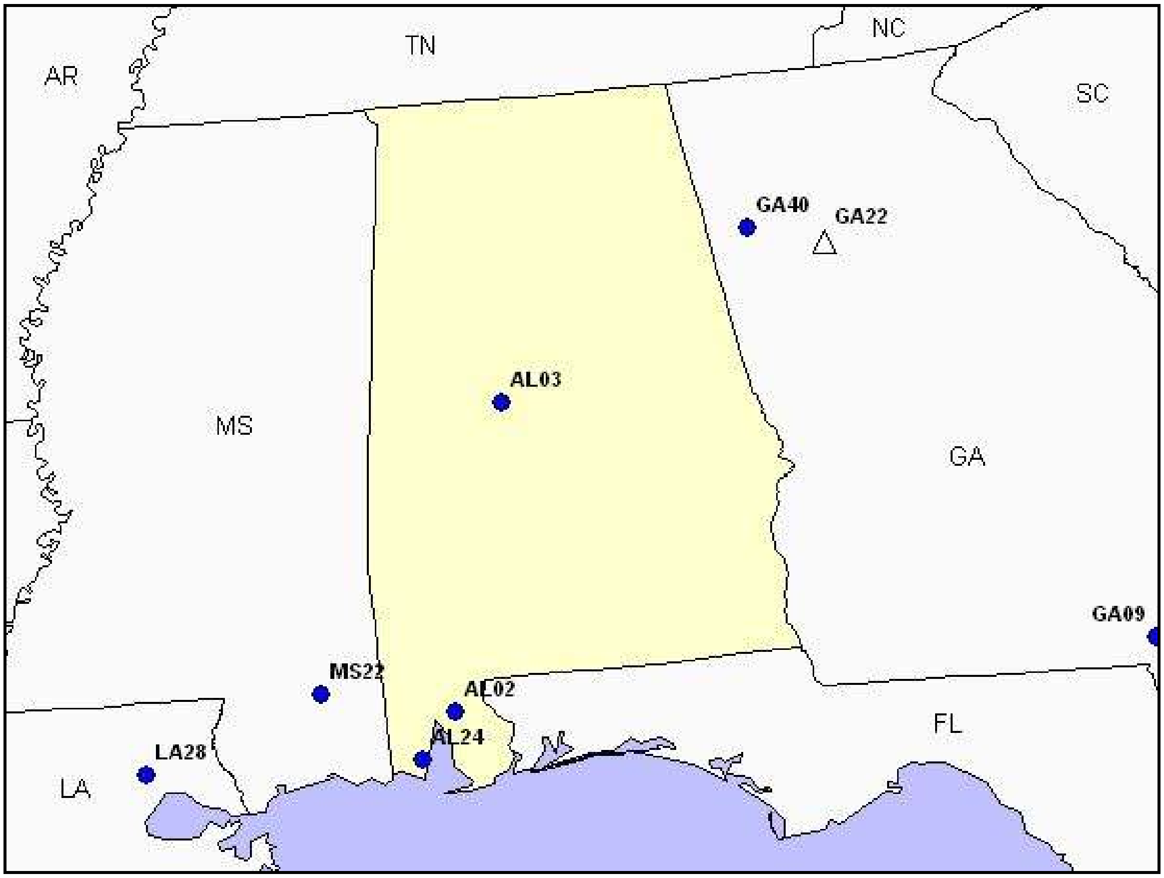

Figure 4. Map of locations of MDN sampling sites in the southeastern region of the United States. Data from sites AL02 and AL24 were used for analysis of Hg deposition near Weeks Bay.

Seasonal variations in mercury deposition were studied over a period of one year from January, 2003, to March, 2004 (Lindberg and Vermette, 1995). In addition to MDN site data, USGS precipitation data were also collected from two rain gauges on the Fish River and Magnolia River (USGS Waterdata). These two data sets were graphed together to establish possible correlations that may exist between precipitation and mercury deposition.

Surface Water and Groundwater Sampling

Four research trips were taken to the Weeks Bay watershed from July, 2005, to May, 2006. Water-chemistry data were collected from the bay and from nearby USGS monitoring wells WW13, WW14, WW15, and WW16 (Fig. 5). These USGS monitoring wells were drilled in clusters of two in a small area along the west bank of Weeks Bay. The clustered wells were completed at different depths, which enable the examination of changes in hydraulic head with depth. The water-table elevations of the wells were measured to determine vertical hydraulic gradients. An upward gradient would indicate that groundwater flow has an upward component as it discharges into the bay. Water-chemistry data were collected from the USGS wells using the multi-parameter TROLL 9000 (manufactured by In-Situ, Inc.). The wells were bailed by removing three well volumes before sampling to insure that a representative groundwater sample was collected (EPA, 1995). To study water table and tidal fluctuations a multi-parameter TROLL 8000 was left in WW16 for a 24-hour period to record water-pressure changes. Using a boat provided by the Weeks Bay National Estuary Research Reserve

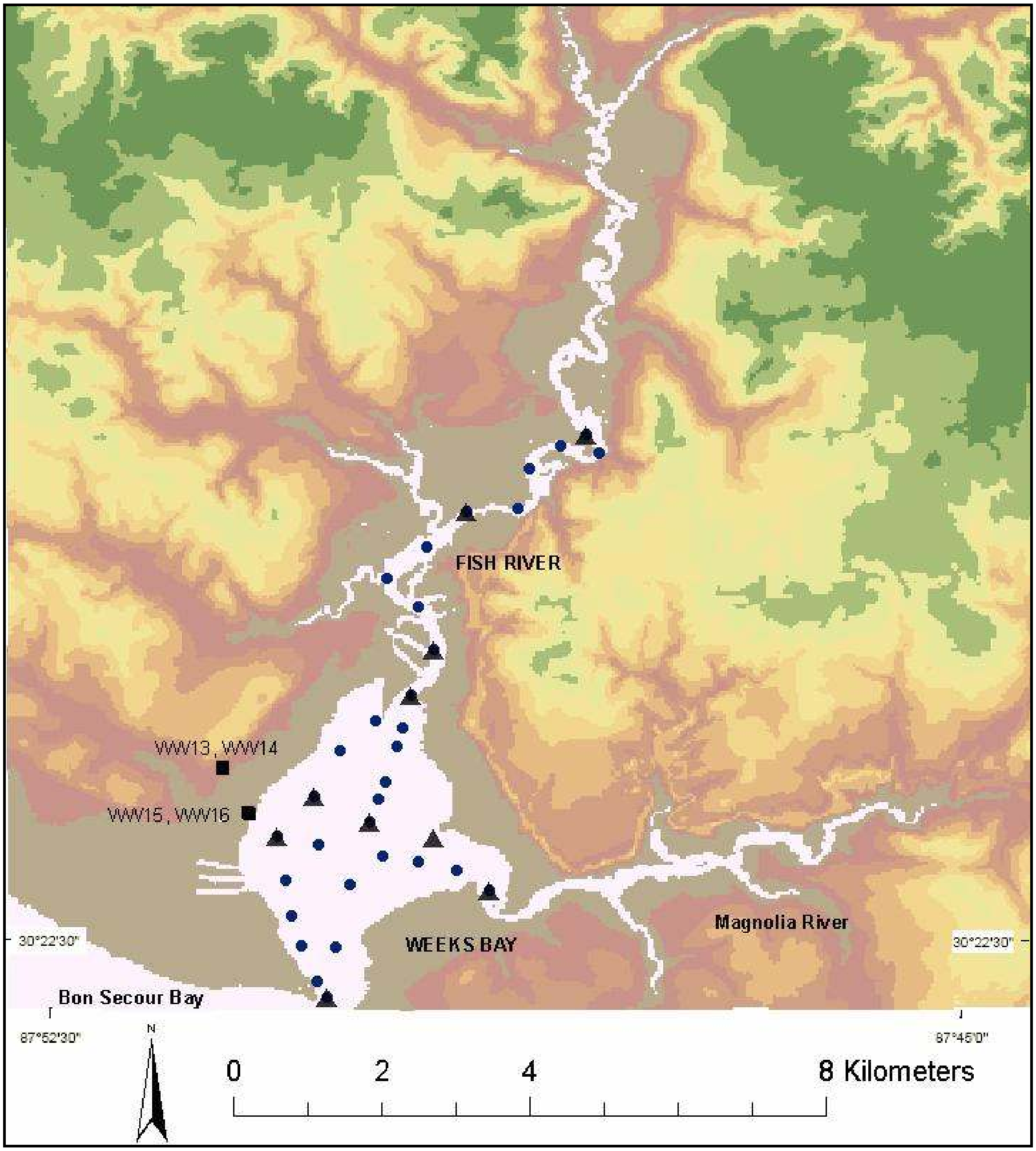

Figure 5. Digital elevation map of Weeks Bay with sampling locations and USGS monitoring wells. The blue circles represent areas where field chemistry data was collected while the black triangles represent areas where water samples were collected for major ion, trace element and isotope analysis.

(WBNERR), water-chemistry data were collected from 32 locations throughout the bay (Fig 5). Measurements were repeated at the same locations for each field trip to find seasonal variations. A Garmin GPSMAP CS60 was used to ensure sampling points were consistent during repeated trips. Water chemistry data, including temperature, pH, specific conductance, dissolved oxygen (DO), oxidation reduction potential (ORP), and turbidity were collected using the multi-parameter TROLL 9000 at each location at different water column depths to study their spatial changes. The data were recorded at half-meter depth intervals until bay bottom sediments were reached. In addition to water-chemistry data, ten water samples were collected from the bay for laboratory chemical and isotope analysis (Fig. 5). Using a sampler, 150 ml bottles were lowered and filled near river and bay bottom.

Laboratory Geochemical Analyses

Samples collected from groundwater, bay water, and river water were sent for geochemical and stable isotope analyses to study the source and evolution of various waters in the Weeks Bay watershed. Oxygen, hydrogen and carbon isotopic ratios were measured using the Finnigan Mat delta PLUS XP Mass Spectrometer at Florida State University. The analysis of DOC was conducted in the Civil Engineering Water Quality Laboratory at Auburn University. A raw and an acidified sample from each water well and surface water locations were sent to ACTLABS for major ion and trace element analysis using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Optical Emission Spectrometer (ICP-OES). Anion concentrations were measured in the ACTLABS using Dionex 2000 Ion Chromatograph (IC).

Computer Modeling and Visualization

The collected and analyzed data were then graphed and plotted to provide a visual representation of mixing processes occurring within Weeks Bay. ArcGIS, Excel, Surfer, and Tecplot were all used to accomplish this. An ArcGIS base map was created using a digital elevation model of the USGS Magnolia Spring Quadrangle. Surface-water and groundwater sampling locations were plotted using the GPS measurements from the field.

Transects of Weeks Bay water chemistry were created at various depths using Excel to plot the parameters collected by the In-Situ probes. The oxygen and hydrogen isotopic ratios of water relative to the Local Mean Water Line (LMWL) and seawater were analyzed using Tecplot to determine the effects of mixing and evaporation on water chemistry and salinity. The graphs created from Techplot were used for comparing and correlating water chemistry parameters spatial variations in order to find relationships.

Spatial variations of water-chemistry parameters within the bay and river were determined using Surfer. Color and contour maps for water-chemistry field parameters were generated at different depths. These maps could be compared to find trends, thermal and salinity stratification, and mixing zones within the bay and river. Hg speciation at various Eh-pH conditions was analyzed using Geochemist's Workbench (Bethke, 1996).

MERCURY DEPOSTION AND WATER CHEMISTRY IN THE WEEKS BAY WATERSHED

The following sections present data related to major ion chemistry, trace elements content, and isotopic composition of waters collected within the Weeks Bay watershed. The results obtained in this study were comprised of data from the MDN as well as field sampling and laboratory analyses. The data can be used to understand the complex interrelationships of bay, ground, and surface waters taking place within Weeks Bay and the effects of these interactions on water chemistry and mercury methylation.

Mercury Deposition

Table 1 shows data collected by the NADP MDN at the Alabama site the AL02 near Mobile Bay. This table lists the weekly deposition (ng/L) and concentration values of total mercury (ng/m^2) in precipitation collected from January, 2003, to March, 2004. Mercury deposition and concentration values were also analyzed from NADP's MDN site AL24 (Table 2) over a twelve month period from January, 2003, to January, 2004, with the same parameters recorded at site AL02. Both NADP MDN sites show seasonal trends of mercury deposition throughout the analyzed collection period with highest deposition occurring during June and July months and lowest mercury deposition occurring from November to January.

Table 1. Data from NADP MDN site AL02 showing Hg concentration and deposition from January 2003 to March 2004.

Site ID	Date On	Date Off	Total Hg Concentration (ng/L)	Total Hg Wet Deposition (ng/m²)
AL02	12/30/2002 14:24	1/7/2003 19:51	3.74	285.14
AL02	1/7/2003 19:57	1/14/2003 12:49	--	0
AL02	1/14/2003 12:53	1/21/2003 14:13	--	0
AL02	1/21/2003 14:18	1/28/2003 14:36	--	--
AL02	1/28/2003 14:45	2/4/2003 14:13	10.23	70.21
AL02	2/4/2003 14:20	2/11/2003 15:03	9.35	142.49
AL02	2/11/2003 15:06	2/18/2003 16:01	12.09	322.62
AL02	2/18/2003 16:08	2/25/2003 14:48	9.04	597.13
AL02	2/25/2003 15:06	3/4/2003 14:10	5.4	382.81
AL02	3/4/2003 14:17	3/11/2003 15:27	14.36	857.38
AL02	3/11/2003 15:32	3/17/2003 15:45	16.6	928.05
AL02	3/17/2003 15:57	3/25/2003 17:40	--	--
AL02	3/25/2003 17:43	4/1/2003 15:57	16.74	93.58
AL02	4/1/2003 16:09	4/8/2003 14:55	11.16	1063.08
AL02	4/8/2003 15:00	4/15/2003 13:10	8.54	238.74
AL02	4/15/2003 13:20	4/22/2003 13:02	11.9	86.74
AL02	4/22/2003 13:11	4/29/2003 15:05	14.39	347.42
AL02	4/29/2003 15:11	5/6/2003 13:05	23.59	59.94
AL02	5/6/2003 13:10	5/13/2003 13:15	14.38	54.78
AL02	5/13/2003 13:17	5/20/2003 15:05	10.37	2308.71
AL02	5/20/2003 15:12	5/27/2003 15:00	6.46	1050.3
AL02	5/27/2003 15:10	6/3/2003 14:03	14.36	430.42
AL02	6/3/2003 14:05	6/10/2003 16:06	3.84	859.21
AL02	6/10/2003 16:12	6/17/2003 15:22	11.68	816.12
AL02	6/17/2003 15:27	6/24/2003 18:58	9.17	1010.86
AL02	6/24/2003 19:05	7/1/2003 18:39	13.53	3667.41
AL02	7/1/2003 18:45	7/8/2003 18:03	17.17	1252.02
AL02	7/8/2003 18:08	7/15/2003 16:35	--	--
AL02	7/15/2003 16:38	7/22/2003 15:29	16.35	1939.64
AL02	7/22/2003 15:40	7/29/2003 16:00	11.97	1368.97
AL02	7/29/2003 16:05	8/5/2003 12:20	18.87	906.01

Table 1. Continued.

Site ID	Date On	Date Off	Total Hg Concentration (ng/L)	Total Hg Wet Deposition (ng/m²)
AL02	8/5/2003 12:30	8/12/2003 13:55	20.61	492.29
AL02	8/12/2003 14:01	8/19/2003 16:09	11.5	306.75
AL02	8/19/2003 16:13	8/26/2003 16:07	23.41	624.53
AL02	8/26/2003 16:10	9/2/2003 16:34	123.39	689.5
AL02	9/2/2003 16:40	9/9/2003 13:06	20.45	587.09
AL02	9/9/2003 13:12	9/16/2003 18:33	32.91	585.3
AL02	9/16/2003 18:39	9/23/2003 15:43	19.87	514.79
AL02	9/23/2003 15:48	9/30/2003 17:09	--	--
AL02	9/30/2003 17:19	10/7/2003 16:59	--	0
AL02	10/7/2003 17:04	10/14/2003 18:47	5.04	202.34
AL02	10/14/2003 18:51	10/21/2003 13:00	--	0
AL02	10/21/2003 13:05	10/28/2003 13:54	8.86	562.86
AL02	10/28/2003 14:00	11/4/2003 13:45	--	0
AL02	11/4/2003 13:55	11/10/2003 21:35	6.29	47.99
AL02	11/10/2003 21:42	11/18/2003 16:10	11.12	5.65
AL02	11/18/2003 16:10	11/25/2003 16:00	7.33	212.3
AL02	11/25/2003 16:05	12/2/2003 17:05	7.38	628.04
AL02	12/2/2003 17:10	12/9/2003 12:50	5.76	102.53
AL02	12/9/2003 12:57	12/16/2003 13:10	5.6	273.49
AL02	12/16/2003 13:16	12/23/2003 19:35	--	0
AL02	12/23/2003 19:39	12/30/2003 18:25	5.14	359.3
AL02	12/30/2003 18:27	1/6/2004 13:05	9.45	19.2
AL02	1/6/2004 13:12	1/13/2004 14:20	10.04	114.79
AL02	1/13/2004 14:26	1/20/2004 17:25	3.43	156.82
AL02	1/20/2004 17:34	1/27/2004 12:47	8.03	397.97
AL02	1/27/2004 12:55	2/3/2004 13:05	8.87	83.38
AL02	2/3/2004 13:15	2/10/2004 12:30	8.71	189.56
AL02	2/10/2004 12:40	2/17/2004 13:15	8.44	845.73
AL02	2/17/2004 13:25	2/23/2004 18:30	16.61	251.58
AL02	2/23/2004 18:32	3/2/2004 12:50	4.51	309.97
AL02	3/2/2004 12:59	3/9/2004 13:58	14.64	100.42
AL02	3/9/2004 14:07	3/16/2004 12:20	9.33	142.26
AL02	3/16/2004 12:28	3/23/2004 18:03	--	0
AL02	3/23/2004 18:03	3/30/2004 13:29	--	--

Table 2. Data from NADP MDN site AL24 showing Hg concentration and deposition from January 2003 to January 2004.

Site ID	Date On	Date Off	Total Hg Concentration (ng/L)	Total Hg Wet Deposition (ng/m²)
AL24	12/30/2002 15:08	1/7/2003 14:40	5.77	341.34
AL24	1/7/2003 14:45	1/14/2003 17:33	--	0
AL24	1/14/2003 17:38	1/21/2003 16:00	--	0
AL24	1/21/2003 16:03	1/28/2003 16:42	--	0
AL24	1/28/2003 16:44	2/4/2003 14:51	3.98	32.36
AL24	2/4/2003 14:53	2/11/2003 16:08	7.78	128.46
AL24	2/11/2003 16:10	2/18/2003 16:50	8.14	140.64
AL24	2/18/2003 16:52	2/25/2003 17:15	5.22	493.22
AL24	2/25/2003 17:20	3/4/2003 22:55	5.58	513.43
AL24	3/4/2003 22:57	3/11/2003 15:46	15.21	216.47
AL24	3/11/2003 15:48	3/17/2003 17:13	7.37	619.96
AL24	3/17/2003 17:16	3/25/2003 16:31	--	0
AL24	3/25/2003 16:34	4/1/2003 16:32	17.4	66.3
AL24	4/1/2003 16:35	4/8/2003 21:36	12.4	677.54
AL24	4/8/2003 21:39	4/15/2003 16:52	5.76	5.85
AL24	4/15/2003 16:55	4/22/2003 15:17	8.37	95.74
AL24	4/22/2003 15:20	4/29/2003 17:55	13.41	105.63
AL24	4/29/2003 17:58	5/6/2003 17:52	--	0
AL24	5/6/2003 17:55	5/13/2003 17:38	19.16	272.53
AL24	5/13/2003 17:41	5/20/2003 17:15	8.49	718.77
AL24	5/20/2003 17:19	5/27/2003 15:15	4.47	203.36
AL24	5/27/2003 15:20	6/3/2003 22:31	15.69	111.6
AL24	6/3/2003 22:44	6/10/2003 22:16	7.22	716
AL24	6/10/2003 22:20	6/17/2003 15:57	23.26	407.79
AL24	6/17/2003 16:00	6/24/2003 22:40	10.48	2316.36
AL24	6/24/2003 22:42	7/1/2003 16:50	7.25	1339.37

Table 2. Continued.

Site ID	Date On	Date Off	Total Hg Concentration (ng/L)	Total Hg Wet Deposition (ng/m²)
AL24	7/1/2003 16:54	7/8/2003 19:54	9.21	346.44
AL24	7/8/2003 20:00	7/15/2003 14:50	20.94	393.58
AL24	7/15/2003 14:54	7/22/2003 19:30	15.61	444.21
AL24	7/22/2003 19:33	7/29/2003 15:45	8.49	750.62
AL24	7/29/2003 15:47	8/5/2003 19:38	15.04	676.16
AL24	8/5/2003 19:40	8/12/2003 16:12	16.04	407.59
AL24	8/12/2003 16:14	8/19/2003 16:10	6.75	257.17
AL24	8/19/2003 16:10	8/26/2003 14:18	11.91	381.39
AL24	8/26/2003 14:20	9/2/2003 19:45	17.27	381.63
AL24	9/2/2003 19:48	9/9/2003 14:31	27.78	21.16
AL24	9/9/2003 14:33	9/16/2003 15:55	89.1	113.15
AL24	9/16/2003 15:55	9/23/2003 20:12	22.58	1066.91
AL24	9/23/2003 20:15	9/30/2003 13:42	35.26	8.95
AL24	9/30/2003 13:50	10/7/2003 15:56	--	0
AL24	10/7/2003 15:58	10/14/2003 17:28	4.32	318.8
AL24	10/14/2003 17:30	10/21/2003 14:24	--	0
AL24	10/21/2003 14:26	10/28/2003 20:15	13.68	340.74
AL24	10/28/2003 20:20	11/4/2003 15:36	--	0
AL24	11/4/2003 15:40	11/10/2003 20:35	--	0
AL24	11/10/2003 22:30	11/18/2003 14:50	7.61	17.41
AL24	11/18/2003 14:52	11/25/2003 19:52	5.91	169.65
AL24	11/25/2003 19:55	12/2/2003 19:58	7.06	281.77
AL24	12/2/2003 20:00	12/9/2003 16:30	6.47	231.89
AL24	12/9/2003 16:30	12/16/2003 15:12	5.01	155.43
AL24	12/16/2003 15:15	12/23/2003 18:15	--	0
AL24	12/23/2003 18:18	12/30/2003 19:30	--	--
AL24	12/30/2003 19:32	1/6/2004 15:10	19.36	83.63
AL24	1/6/2004 15:15	1/13/2004 20:40	8.61	124.65
AL24	1/13/2004 20:45	1/20/2004 16:35	4.11	267.37
AL24	1/20/2004 16:40	1/27/2004 16:50	--	--
AL24	1/27/2004 16:55	2/3/2004 17:00	15.59	103

Surface-Water Chemistry

Data from sampling surface-water is shown in Table 3 and records latitude/longitude, temperature, pH, ORP, conductivity, DO, and turbidity data from the July, 2005, research trip, data from additional trips can be found in the appendix (see attached CD). Measurements were taken at different depths to delineate possible thermal and haline stratifications. River water and surface water near the river mouth are characterized by relatively low pH (5.99 to 6.54), low temperature (27.80ºC to 31.65ºC), and low conductivity (138 µS/cm to 2017 µS/cm). In contrast, surface waters near the bay mouth have relatively high pH (7.8 to 8.75), high temperature (32.0°C to 33.25°C), and high conductivity (3350 µS/cm to 5706 µS/cm). In general, surface water sampled near the river mouth where river water mixes with bay water has the lowest DO or ORP values The major ion, trace metals, and DOC contents of surface waters are shown in Table 4, complete ICP-MS, ICP-OES, and IC table can be found in the appendix (see attached CD). Surface waters generally have a lower metal content and high chlorine, sodium, and sulfate concentrations.

Groundwater Chemistry

Temperature, pH, ORP, conductivity, DO, and turbidity were measured from groundwater taken from the four USGS monitoring wells (Table 5). The pH and temperature of the water in the monitoring wells were generally lower (4.53 to 6.04 and 20.6°C to 26.1°C, respectively) than those of bay water. Conductivity was also low, in the monitoring wells. The deep well closest to the Bay, WW15, however, recorded higher conductivity measurements (4688µS/cm) with respect to other wells. Major ion

Table 3. Surface water chemistry from locations within Weeks Bay and Fish River taken at surface level and one-meter depth during July, 2005. See Fig. 5 for sample locations.

Sample ID	Location	GPS ID	Temperature (°C)	pH	ORP (mV)	Conductivity (uS/cm)	DO (ug/L)	Turbidity (NTU)
WB1-S	30.413306/87.825500	009	30.93	6.47	540	909	5950	22.4
WB1-1	30.413306/87.825500	009	30.16	6.3	632	950	7125	30.2
WB2-S	30.409472/87.826583	010	31.65	6.41	609	942.6	5020	22.5
WB2-1	30.409472/87.826583	010	27.80	5.99	646	219	2930	100
WB9-S	30.407222/87.827361	017	32.17	6.38	502	204	6233	22
WB9-0.75	30.407222/87.827361	017	28.71	6.06	541	217.1	3970	28.6
WB7-S	30.402861/87828694	015	31.50	6.28	488	300	4455	19.8
WB7-0.75	30.402861/87828694	015	31.24	7.19	455	2800	6031	NA
WB8-S	30.400806/87.829639	016	32.16	6.6	518	1311	5498	19.7
WB8-0.8	30.400806/87.829639	016	31.82	8.45	344	4235	6220	NA
WB6-S	30.398083/87.830611	014	33.02	8.43	384	2715	6360	23.3
WB6-1	30.398083/87.830611	014	31.89	8.29	361	5147	5879	NA
WB5-S	30.390417/87.833083	013	33.56	8.77	493	5174	8100	17.6
WB5-1	30.390417/87.833083	013	32.13	8.58	515	5630	7080	27.8
WB4-S	30.382889/87.834806	012	32.89	8.6	467	5522	7394	21.6
WB4-1	30.382889/87.834806	012	32.36	8.5	518	5706	6790	31.1
WB3-S	30.376861/87.835806	011	32.82	8.49	533	5700	6700	19.9
WB3-1	30.376861/87.835806	011	32.76	8.45	558	5444	6900	26
WB10-S	30.389639/87.816167	028	32.00	7	457	3000	5038	29
WB10-0.75	30.389639/87.816167	028	31.70	7.19	455	3254	5116	77.5
WB11-S	30.392194/87.820056	029	32.66	8.09	432	3975	6330	28.2
WB11-1	30.392194/87.820056	029	32.19	7.8	437	4296	5537	NA
WB12-S	30.393194/87.824694	030	32.60	8.62	381	4002	7360	24.1
WB12-1	30.393194/87.824694	030	32.25	8.28	414	4616	5357	34.2
WB13-S	30.393889/87.829083	031	33.17	8.66	365	5136	6110	19.8
WB13-1	30.393889/87.829083	031	32.43	8.36	370	5442	5388	29.6
WB14-S	30.395250/87.836778	032	32.66	8.3	356	2340	6658	18
WB14-1	30.395250/87.836778	032	32.40	8.23	404	4860	5224	41.7
WB15-S	30.396850/87.841750	033	32.69	8.06	361	1865	7150	31
WB15-1	30.396850/87.841750	033	32.18	7.8	422	3985	5256	41.6
WB16-S	30.390917/87.840861	034	33.06	8.41	344	2880	6800	19.9
WB16-1	30.390917/87.840861	034	32.11	8.18	397	3981	6057	30.6
WB17-S	30.386694/87.840139	035	33.22	8.75	327	3350	7356	23.3
WB17-1	30.386694/87.840139	035	32.10	8.28	400	4980	5241	38.5
WB18-S	30.383028/87.838944	036	33.22	8.79	324	3255	7746	21
WB18-1	30.383028/87.838944	036	32.08	8.25	387	5056	5572	44
WB19-S	30.378444/87.837056	037	33.25	8.8	330	3436	7815	20.9
WB19-1	30.378444/87.837056	037	32.38	8.4	394	5636	5942	30.1
WB20-S	30.401222/87.837389	038	33.63	8.19	290	2108	7255	24.4
WB20-1	30.401222/87.837389	038	32.46	7.92	346	3676	5543	47.6
WB21-S	30.406722/87.834222	039	32.72	6.69	386	560	5369	26.2
WB21-1	30.406722/87.834222	039	30.50	6.64	402	1180	4193	42.5
WB22-S	30.410306/87.829889	040	31.99	7.03	409	1119	7150	29.9
WB22-1	30.410306/87.829889	040	28.61	6.23	473	330	3020	34.2
Fish1-S	30.445000/87.804333	018	31.40	6.8	403	66.01	8851	9.9
Fish1-1	30.445000/87.804333	018	28.56	6.3	485	60.29	7719	8.9
Fish2-S	30.442722/87.802806	019	31.54	6.63	482	65.31	8805	9.5
Fish2-1	30.442722/87.802806	019	28.50	6.26	526	61.82	7900	8.3
Fish3-S	30.443611/87.807389	020	30.20	6.57	514	63.97	9043	10.7
Fish3-1	30.443611/87.807389	020	29.06	6.29	553	63.04	7762	10.5
Fish4-S	30.440833/87.811306	021	31.98	6.9	455	71.4	9210	13.1
Fish4-1	30.440833/87.811306	021	30.47	6.74	503	66.06	9500	12.4
Fish5-S	30.436000/87.812611	022	31.83	6.98	447	69.26	9500	12.9
Fish5-1	30.436000/87.812611	022	28.81	6.27	530	64.15	7795	10.4
Fish6-S	30.435639/87.818917	023	31.65	6.82	454	76.5	9540	15
Fish6-1	30.435639/87.818917	023	30.11	6.65	489	72.27	9440	14.1
Fish7-S	30.431306/87.823722	024	32.17	6.83	443	98.3	9140	13.9
Fish7-1	30.431306/87.823722	024	31.44	6.6	477	102.5	9000	13.5
Fish8-S	30.427500/87.828556	025	31.97	6.61	444	105.2	8600	14.6
Fish8-1	30.427500/87.828556	025	30.18	6.36	521	88.22	8058	14.5
Fish9-S	30.424111/87.824778	026	32.50	6.7	441	123.3	8659	15.6
Fish9-1	30.424111/87.824778	026	31.71	6.6	496	123.3	8600	15.7
Fish10-S	30.418944/87.822806	027	32.03	6.54	551	201.7	7800	15.6
Fish10-1	30.418944/87.822806	027	30.58	6.27	568	138	7460	15.3

Table 4. Selected major ions and trace metals concentrations of sampled surface waters. Only one surface water site measured detectable mercury levels. Hg levels of sampled waters below detection limits.

Sample ID	Na ppm	Mg ppm	K ppm	Ca ppm	Ni ppb	Br ppm	Rb ppb	Sr ppm	Ba ppb	Cl ppm	Br ppm	F ppm	SO_4^{-2} ppm	HCO_3^- ppm
009	3890	508	142	170	80	22.9	40	2.74	50	7020	55	< 4	925	347
011A	5650	741	221	240	140	33.6	58.2	3.99	40	10400	74	< 5	1360	150
011B	6140	806	232	250	200	36.5	60.4	4.1	40	11200	79	< 5	1460	304
014	--	684	196	210	220	30	51.2	3.53	50	9180	65	< 4	1190	773
018	3420	472	125	150	80	19.7	34.5	2.42	50	6130	47	< 3	809	827
023	3650	479	132	150	80	21.1	38.2	2.54	50	6710	53	< 3	881	110
027	--	322	93	100	60	14.5	25.1	1.73	50	4500	37	< 2	595	891
028	3220	429	124	140	110	19.6	33.3	2.25	50	5960	45	< 3	788	57.2
033	4210	556	157	180	180	25.1	42.6	2.9	50	7720	58	< 4	1010	185
038	4570	604	168	190	200	26.5	45.1	3.1	40	8390	60	< 4	1100	147
041	4860	637	174	190	260	28.1	47.2	3.37	50	8750	60	< 4	1140	409
Seawater	10760	1290	399	411	0.05	67	120	8	10	19350	67	1300	2710	145

Table 5. Groundwater chemistry recorded at USGS monitoring wells WW13, WW14, WW15, and WW16.

Well ID	Temperature (°C)	pH	ORP (mV)	Conductivity (µµS/cm)	DO (µg/L)	Turbidity (NTU)
WW-13	21.9	4.53	365	67.74	7.176	2460.8
WW-14	21.8	4.63	375	63.69	4.884	932.9
WW-15	20.6	4.87	260	50.44	8.411	34
WW-16	26.1	6.04	-9	4688	7.687	779.9

and trace metal analysis from the groundwater samples (Table 6) show higher metal and lower sulfate numbers than those of surface water samples. Mercury levels were above detection limits in three of the monitoring wells, WW13, WW14, and WW16.

Oxygen, Hydrogen, and Carbon Isotopic Signatures

Collected surface water and groundwater samples were sent for stable isotope analysis at Florida State University. $\delta^{18}O$ and δD values (Table 7) are used to determine the source of water and its geochemical evolution in the Weeks Bay watershed. All waters are depleted in ^{18}O and ^{2}H relative to seawater, indicating the strong influence from isotopically-light meteoric water. Groundwater has the lowest $\delta^{18}O$ and δD values. In contrast, Weeks Bay water has the highest $\delta^{18}O$ and δD values. River waters are in the intermediate range between groundwater and bay water.

Carbon within the environment can be a result of several sources, which include; organic material, atmospheric CO_2, CO_2 gas from biologic activity, and the dissolution of carbonate material. Stable carbon isotopic signatures are based on ^{12}C and ^{13}C values, the resulting ratios can help determine carbon sources (Fetter, 2001). Bay and river waters from the Weeks Bay watershed have negative DOC $\delta^{13}C$ ranging from -23.6 $^{0}/_{00}$ to -26.0 $^{0}/_{00}$. The monitoring wells reported no $\delta^{13}C$ values except for WW15 which showed values similar to those found within the bay and rivers.

Table 6. Selected major ions and trace metal concentrations of groundwater from USGS clustered monitoring wells. Two wells, one in each well cluster was found to contain detectable mercury.

Well ID	Na	Mg	Al	Si	K	Fe	Br	Sr	Ba	Hg	Cl	F	SO_4^{-2}	HCO_3^-
	ppm	ppm	ppb	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppm		ppm	ppm
WW13	--	2.46	20	3	0.5	--	--	23.1	71	8	340	< 10	--	364000
WW14	5180	1.06	--	3	0.6	--	30	10.7	36	12	220	< 7	--	418000
WW15	--	131	2900	--	17	30	8500	452	220	--	2610	< 2	100	589000
WW16	--	0.79	--	4	--	--	--	9.3	21	6	--	< 8	--	41400

Table 7. Oxygen, hydrogen, and carbon isotope composition of groundwater, bay water, and river water.

Sample Name	**Water Source**	**$\delta^{18}O$, $^0/_{00}$ (SMOW)**	**δD, $^0/_{00}$ (SMOW)**	**$\delta^{13}C$ (PDB)**	**DOC (ppm)**
9	Transition Zone	-2.1	-14.9	-25.8	2.1
011A	Bay	-1.2	-7.5	-25.2	1.8
011B	Bay	-1	-9.6	-23.6	1.7
14	Bay	-1.5	-10.1	-25.1	1.8
18	River	-2.3	-11.9	n/a	1.7
23	River	-2.2	-15.5	-25.4	1.9
27	River	-2.7	-16.5	-26.0	2
28	Bay	-2.3	-15.6	-25.7	2.2
33	Bay	-1.8	-9.4	-25.0	1.7
38	Bay	-1.6	-8.1	-25.0	1.9
41	Bay	-1.6	-6.3	-25.1	1.4
41	Bay	-1.5	-4.3	-25.3	n/a
WW13	Groundwater	-4.4	-23.1	n/a	1.4
WW14	Groundwater	-4.1	-26.6	n/a	1.9
WW15	Groundwater	-2.7	-17.3	-25.5	3.3
WW16	Groundwater	-4.4	-26.9	n/a	1.7
Sea Water		0	0	0	0.5 – 1.5

DISCUSSION OF CHEMICAL AND HYDROLOGICAL DATA FROM THE WEEKS BAY WATERSHED

The chemistry of Weeks Bay plays a part in the contamination of mercury. In estuary environments these conditions are constantly changing and can affect the severity of contamination. New data from the field study can be added to the results of previous investigators to reveal how the hydrodynamics of Weeks Bay affects water chemistry and mercury methylation. With field data, computer models were created for visual interpretations of water movement and mixing. Chemical and isotope analysis of collected water samples assisted in discovering how water flow and evaporation affected the water chemistry in the watershed. These data sets were analyzed and compared to get a better understanding of the hydrodynamics of Weeks Bay. These different sets of data will be compared to find possible correlations and how they may effect the methylation of mercury in Weeks Bay.

Mercury Deposition and Precipitation

Mercury deposition data from the MDN compared with USGS precipitation data from the same time period show possible correlations between mercury deposition and precipitation for the Weeks Bay watershed (Fig. 6 and 7). USGS precipitation data was collected from the Fish River and the Magnolia River stream gauges, both of which feed into Weeks Bay. Figure 6 shows that total mercury wet deposition increases with the amount of weekly atmospheric precipitation observed near the Fish River. A similar

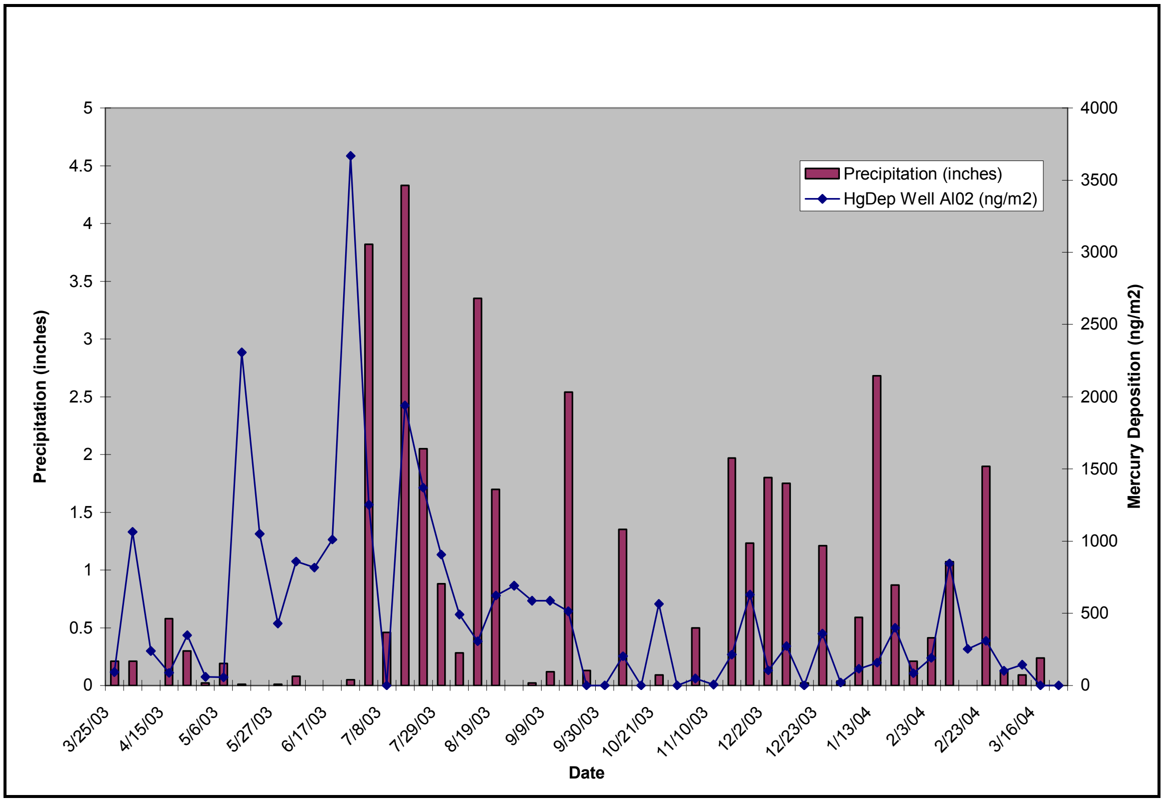

Figure 6. Plot of total mercury wet deposition at site AL02 and weekly atmospheric precipitation observed at the Fish River stream gauge. This correlation suggests that the most likely source for mercury in the Weeks Bay is from atmospheric deposition.

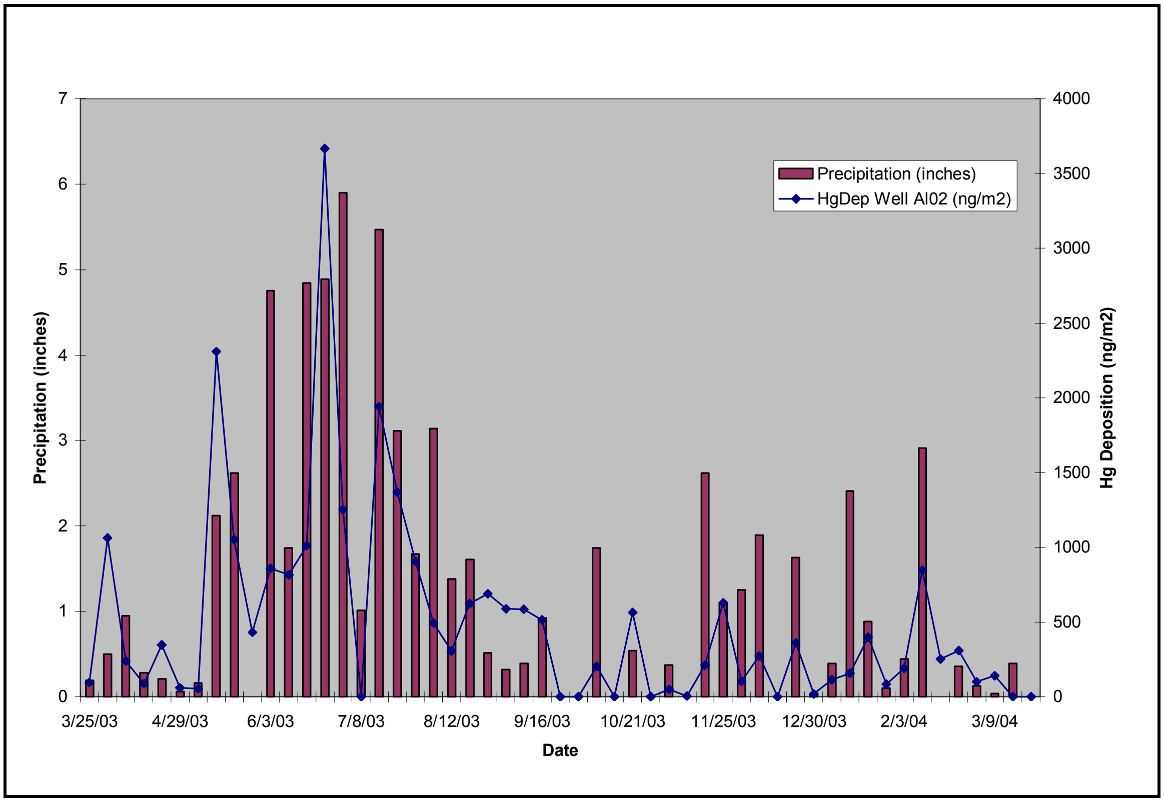

Figure 7. Plot of total mercury wet deposition at site AL02 and weekly atmospheric precipitation observed at the Magnolia River stream gauge that shows similar correlation. Like the Fish River data, these data suggest that the most likely source for mercury in Weeks Bay is from atmospheric deposition.

correlation of mercury wet deposition increase with increased atmospheric precipitation is observed near the Magnolia River (Fig. 7). The correlation of mercury wet deposition and precipitation confirms that the likely source of mercury in Weeks Bay is the result of atmospheric mercury deposition.

Surface-Water Chemistry and Seawater Intrusion

Chemistry data of surface water demonstrates a mixing zone in the Weeks Bay, as a result of seawater intrusion along the bottom of the bay. Grouping of groundwater, river water, and bay water can be seen in the plots relating different water parameters (Fig. 8-11). Waters have distinct characteristics, such as pH, conductivity, DO, and temperature signatures. Groundwater has the lowest temperatures, pH, and conductivity, which would favor Hg methylation (Ullrich et al., 2001; Mason et al., 2006). Surface water near the bay mouth has the highest pH, temperature, and conductivity values. These parameters may help explain the spatial distribution of Hg methylation and its relation to the mixing of seawater, river water, and groundwater in the bay.

A transition zone located at the mouth of the Fish River entering Weeks Bay is indicated by a comparison of data from the groupings of bay and river waters. The pH and conductivity measurements taken along a north-south transect from the mouth of the Fish River to the mouth of Weeks Bay show a trend of saline, high pH seawater entering the bay (Figs. 12 and 13). Water collected from 1m depth has higher pH and conductivity with respect to those collected from the surface. This trend suggests that the seawater intrudes along the bottom portion of the water column in the bay before mixing with acidic freshwater from the Fish River. The trend can also be seen in contour plots of

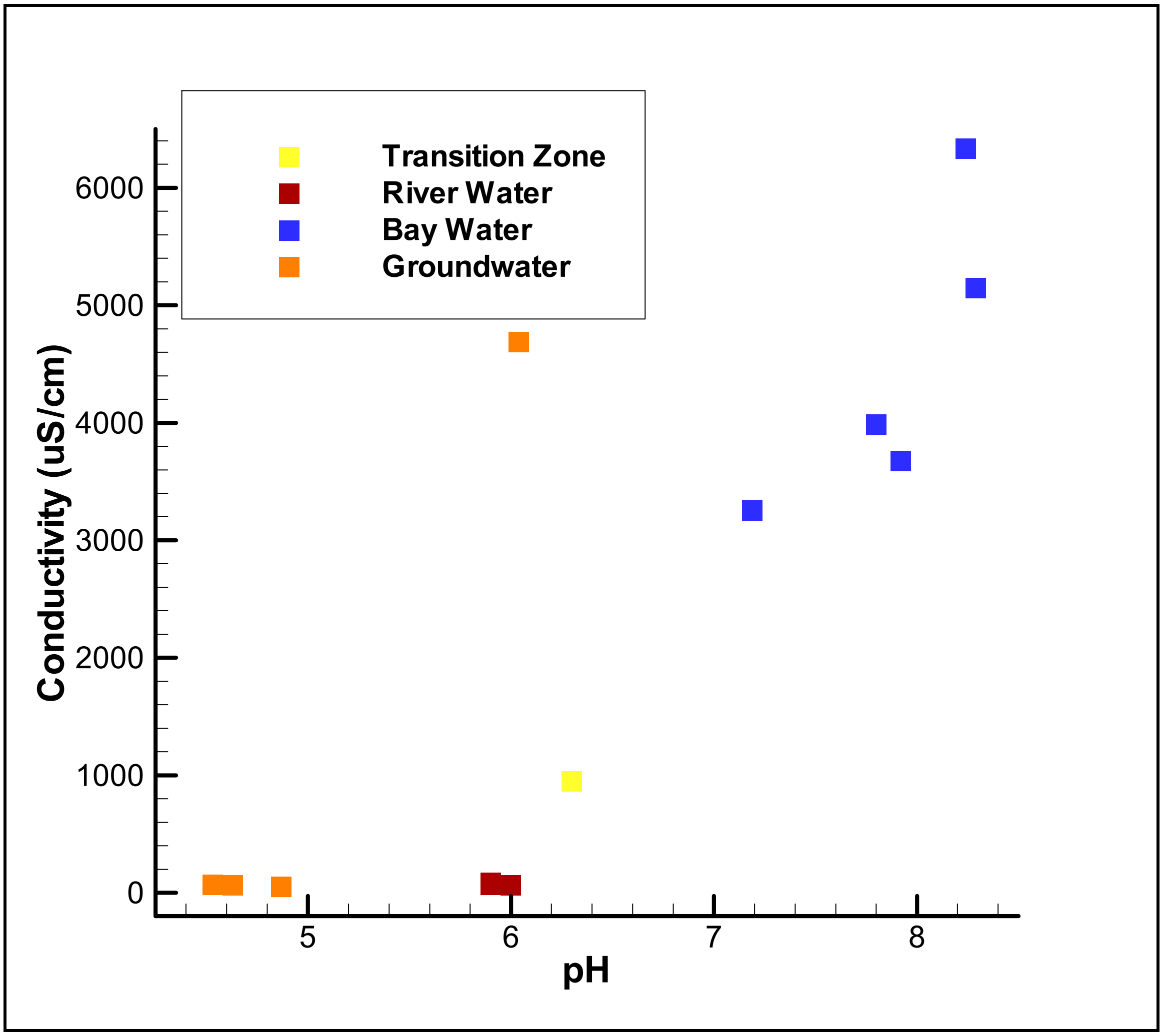

Figure 8. Plot of pH vs. conductivity showing a general relationship in water chemistry parameters that demonstrate the mixing of seawater, river water, and groundwater in Weeks Bay.

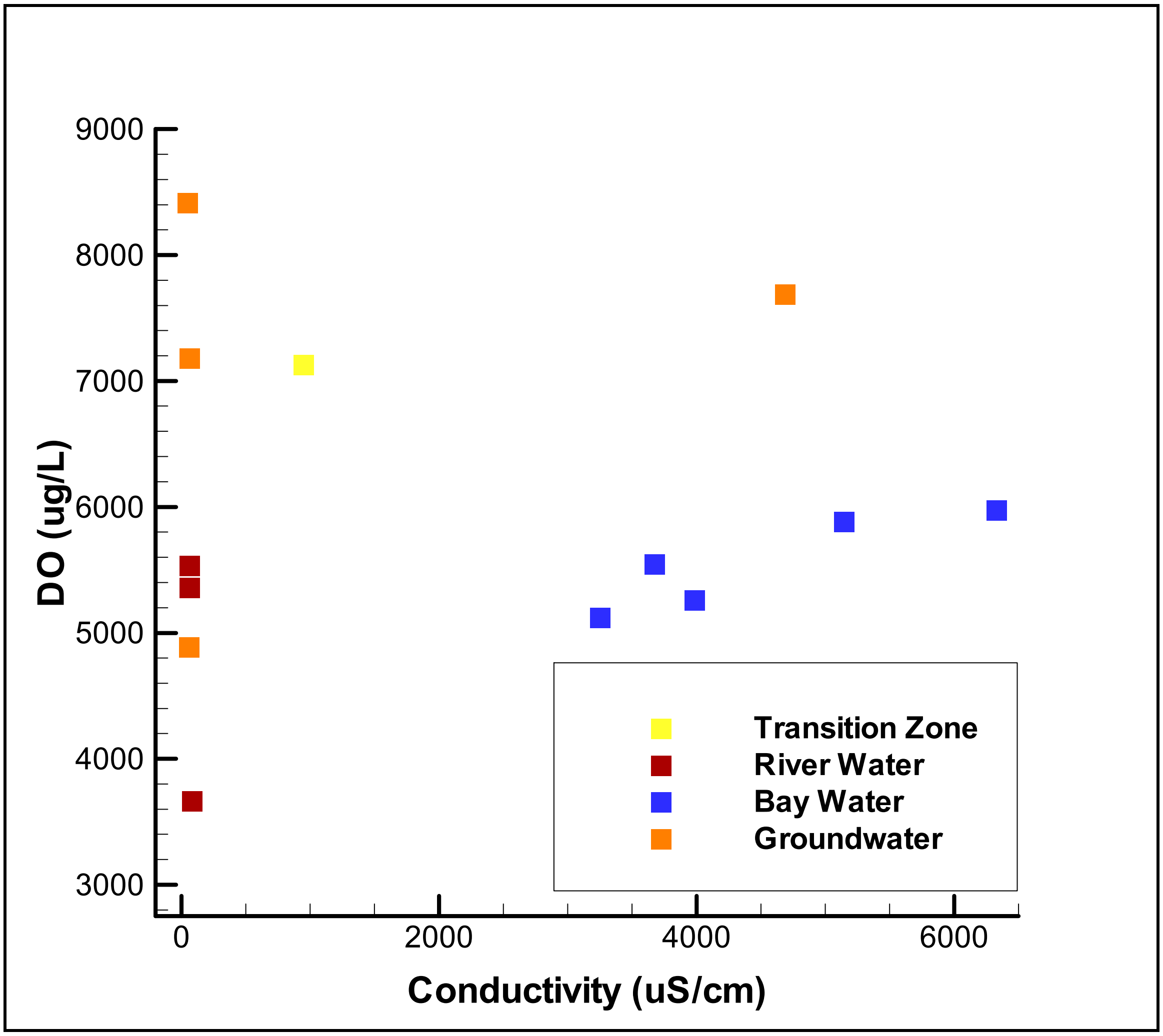

Figure 9. Plot of conductivity vs. DO showing a relationship in water chemistry parameters to locations within Weeks Bay.

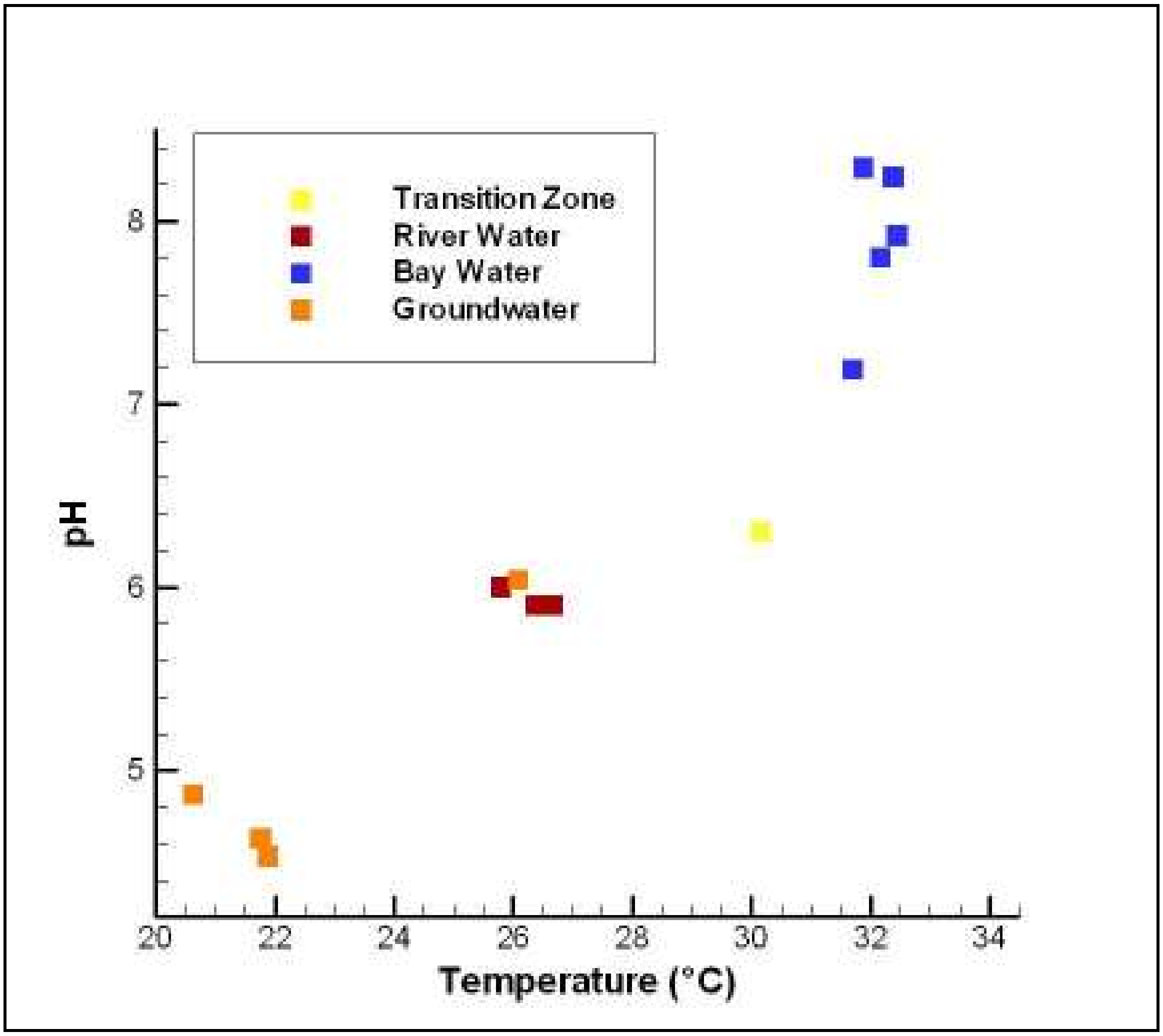

Figure 10. Plot of temperature vs. pH demonstrating a relationship in the mixing of seawater, river water, and groundwater within Weeks Bay.

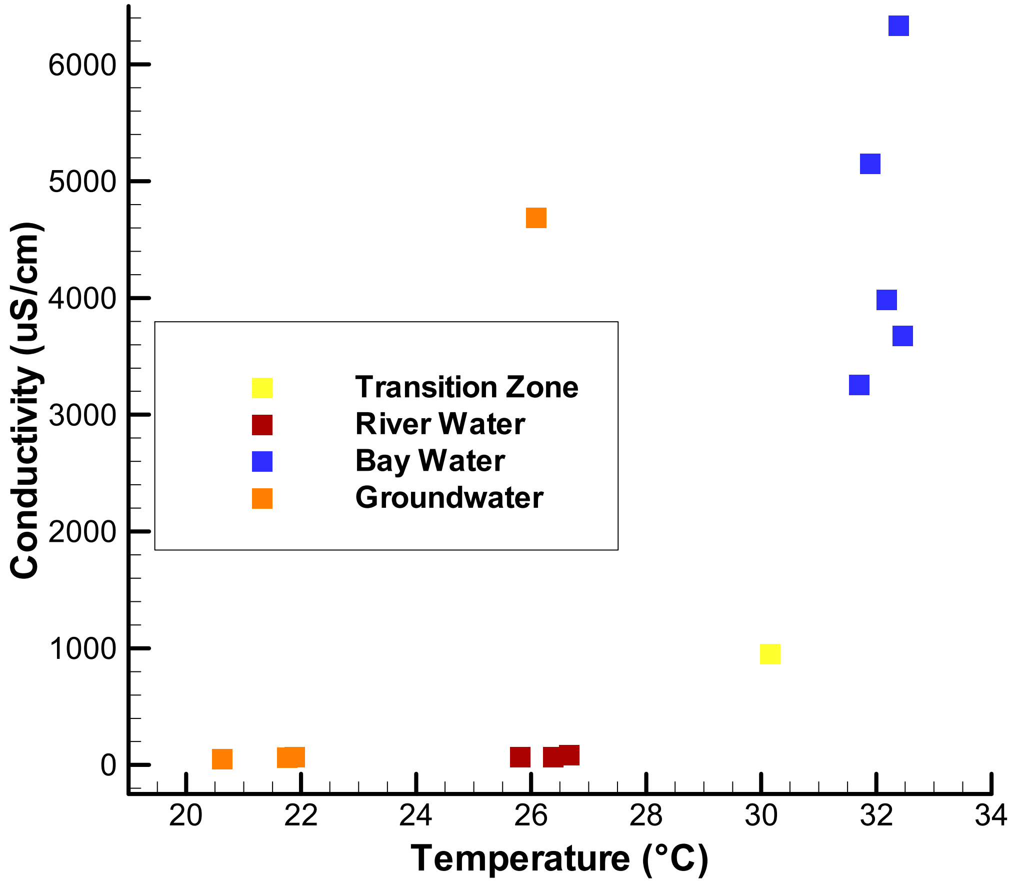

Figure 11. Plot of temperature vs. conductivity that demonstrates a relationship between water chemistry and location within Weeks Bay.

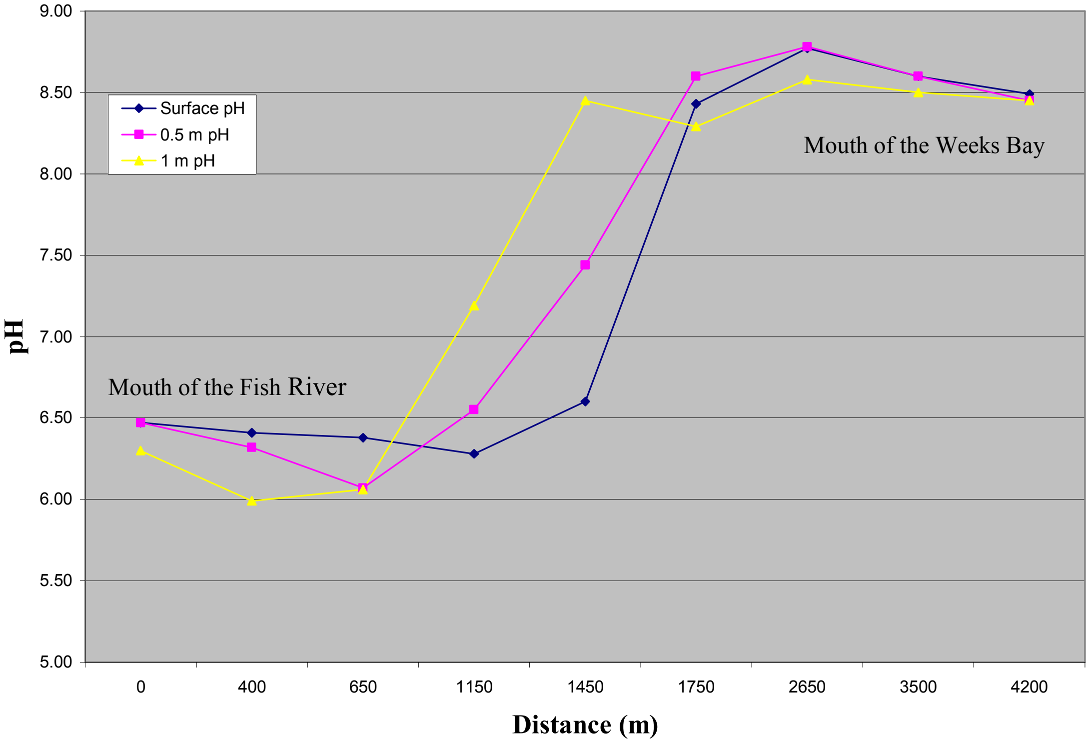

Figure 12. Plot of pH values at three different depths along a north-south transect from the mouth of the Fish River to the mouth of the Weeks Bay. A high pH front is created by the intrusion of seawater into Weeks Bay.

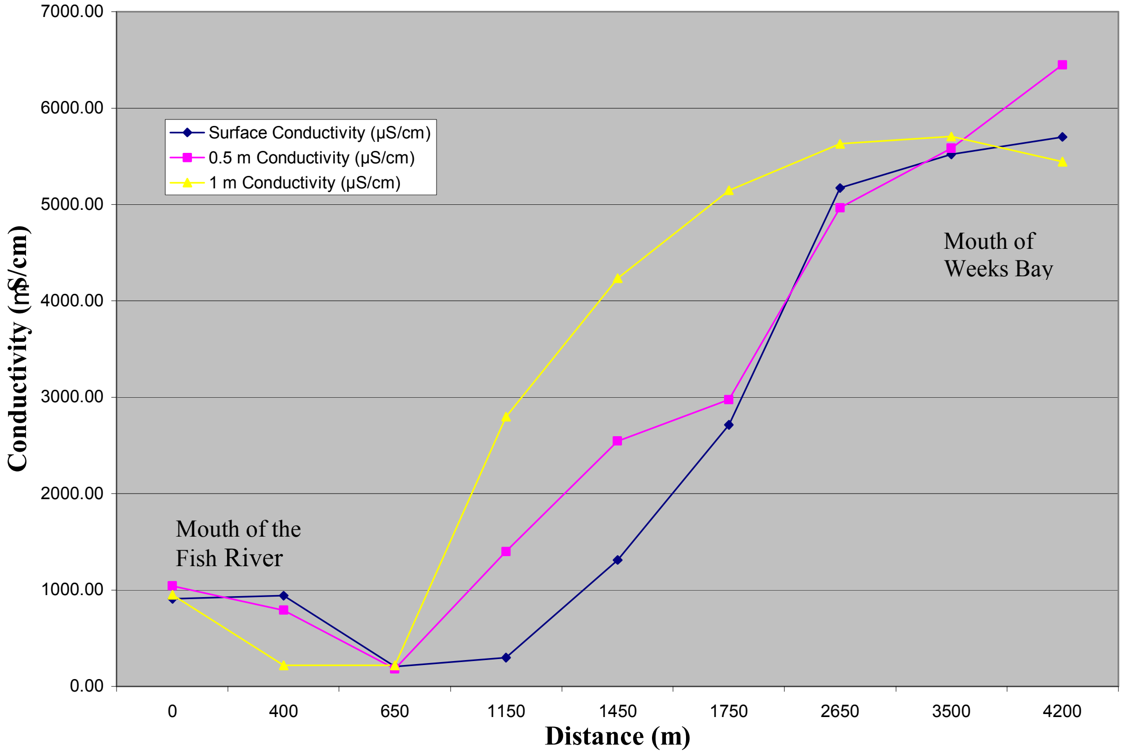

Figure 13. Plot of conductivity values at three different depths along a north-south transect from the mouth of the Fish River to the mouth of the Weeks Bay. A high salinity front, indicated by increasing conductivity, is created by the intrusion of seawater into Weeks Bay.

samples taken at the surface and at 1-meter depths through out the bay (Figs. 14-16). Steep contour gradients of conductivity, temperature, and pH in the upper bay indicate the saline wedge formed by mixing of saltwater and freshwater. Waters at 1 meter depth are more saline than those at the surface, indicating that denser seawater intrudes farther into Weeks Bay at depths below relatively fresh surface water. These plots illustrate that warm dense seawater penetrates beneath cold fresh waters from the rivers in same cases up the mouth of the Fish River, Surfer maps from additional trips can be found in the appendix (see attached CD). The saltwater wedge within Weeks Bay, clearly demonstrates thermal and saline stratification. Interestingly, studies in different watershed basins suggestion that highest mercury methylation mainly occurs near the saline wedge, where acidic water and low-salinity water are both present by mixing (Ullrich et al., 2001; Celo et al., 2005).

Contour maps of DO and ORP for Weeks Bay indicate areas of low oxygen and reducing conditions. The reduced oxygen levels in these areas may indicate microbial activity, which is an important factor in the methylation of mercury. Areas with the lowest DO exist at the mouth of the Fish River near the upper bay. The ORP contour maps show areas of Weeks Bay that exhibit spatial variations in oxidized or reduced conditions (Fig. 18). Some bacteria, such as SRB, prefer anaerobic waters with low ORP values that may contribute to the methylation of mercury (King et al., 2002). Interestingly, the lowest ORP values are located in the upper-central portion of the bay, near the interface of fresh and brackish waters. Additional trips exhibited lower ORP values indicating anaerobic conditions during certain times of the year (see CD). These

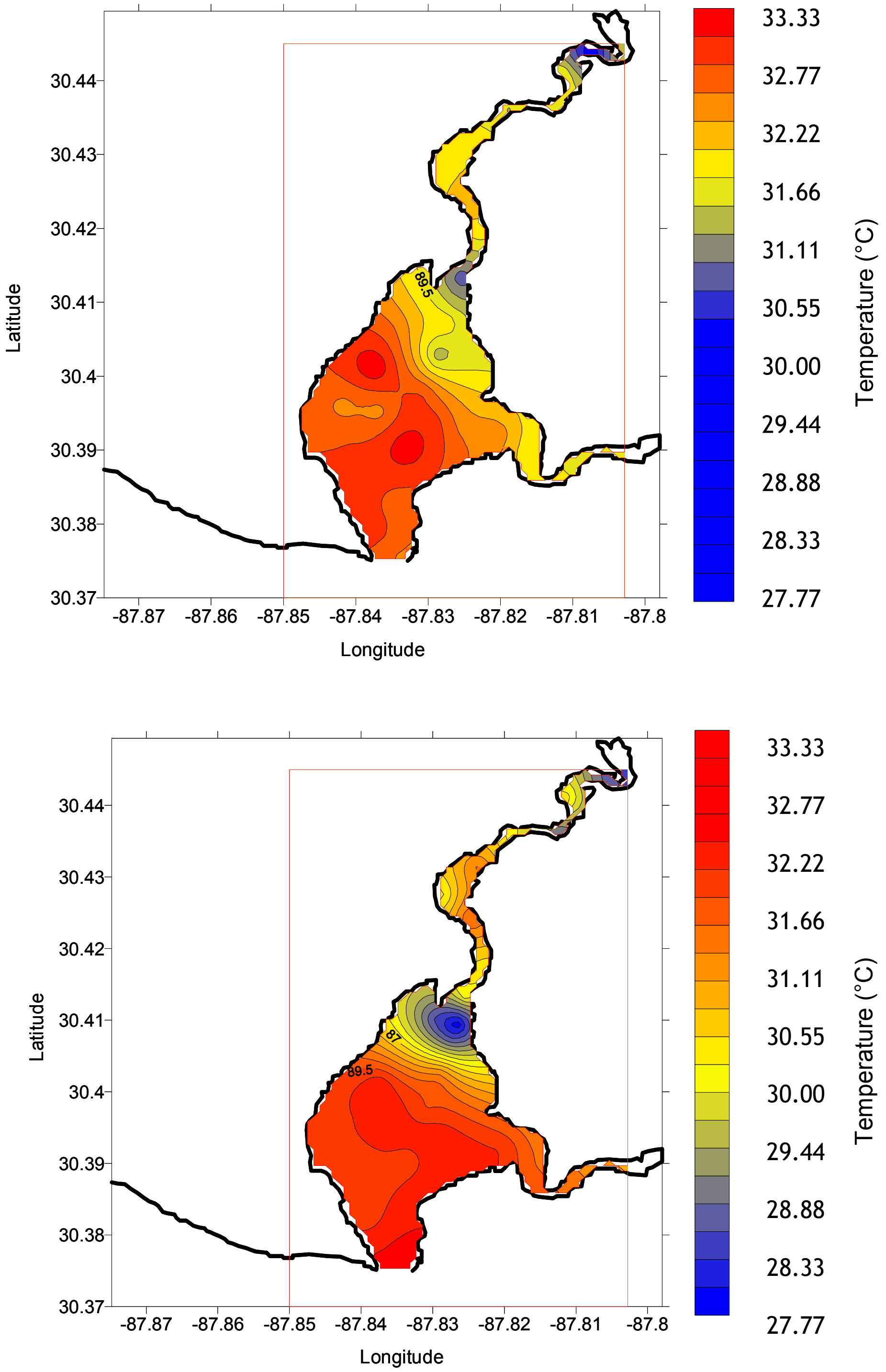

Figure 14. Contour maps of surface (top) and 1-meter (bottom) temperature levels in Weeks Bay and Fish River. Warmer waters at 1-meter depth are shown farther into the bay than those at the surface.

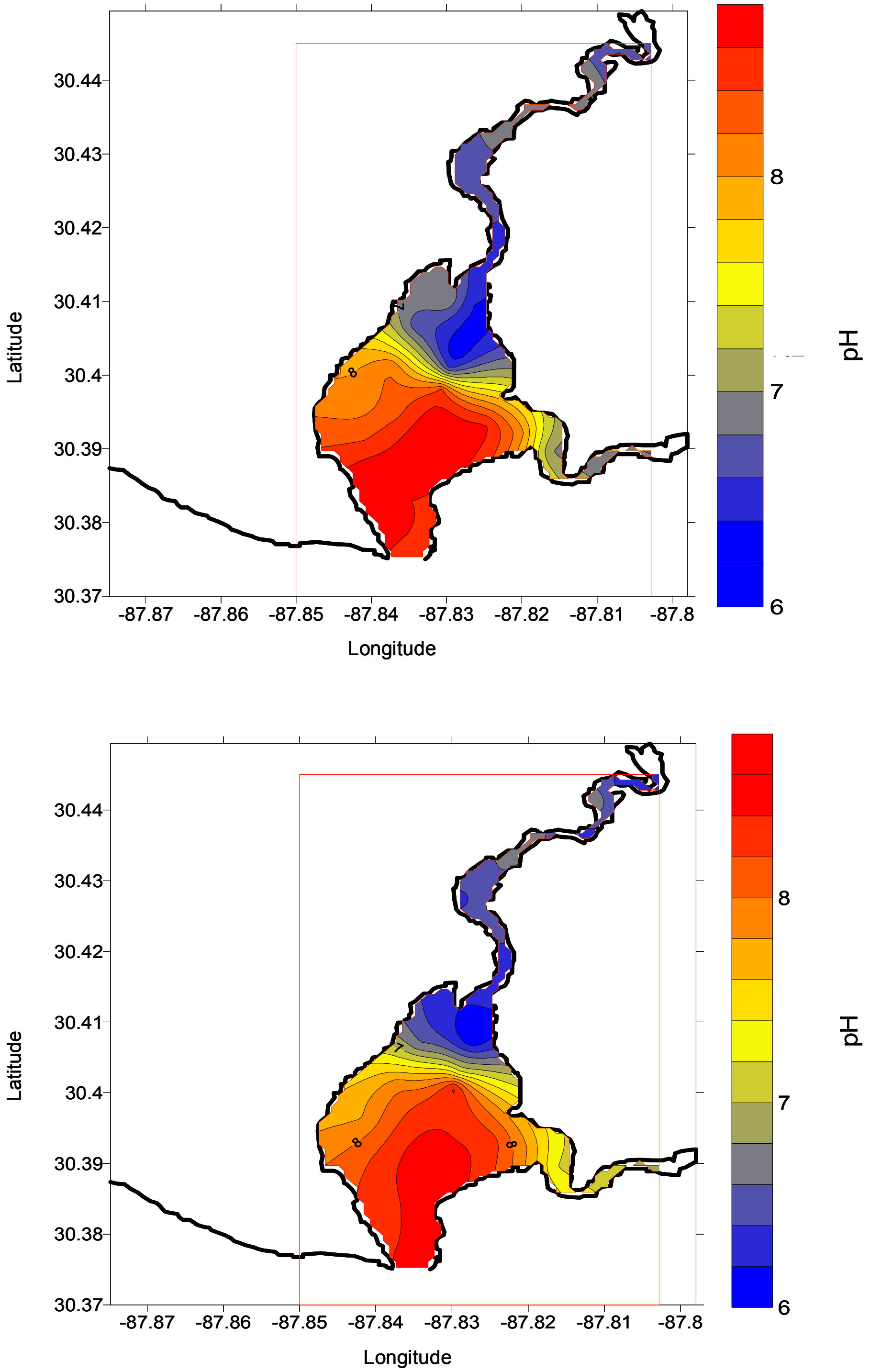

Figure 15. Contour maps of surface (top) and 1-meter (bottom) pH levels in Weeks Bay and Fish River. Like the temperature readings, higher pH water can be found closer to the mouth of the Fish River at 1-meter depth than at the surface.

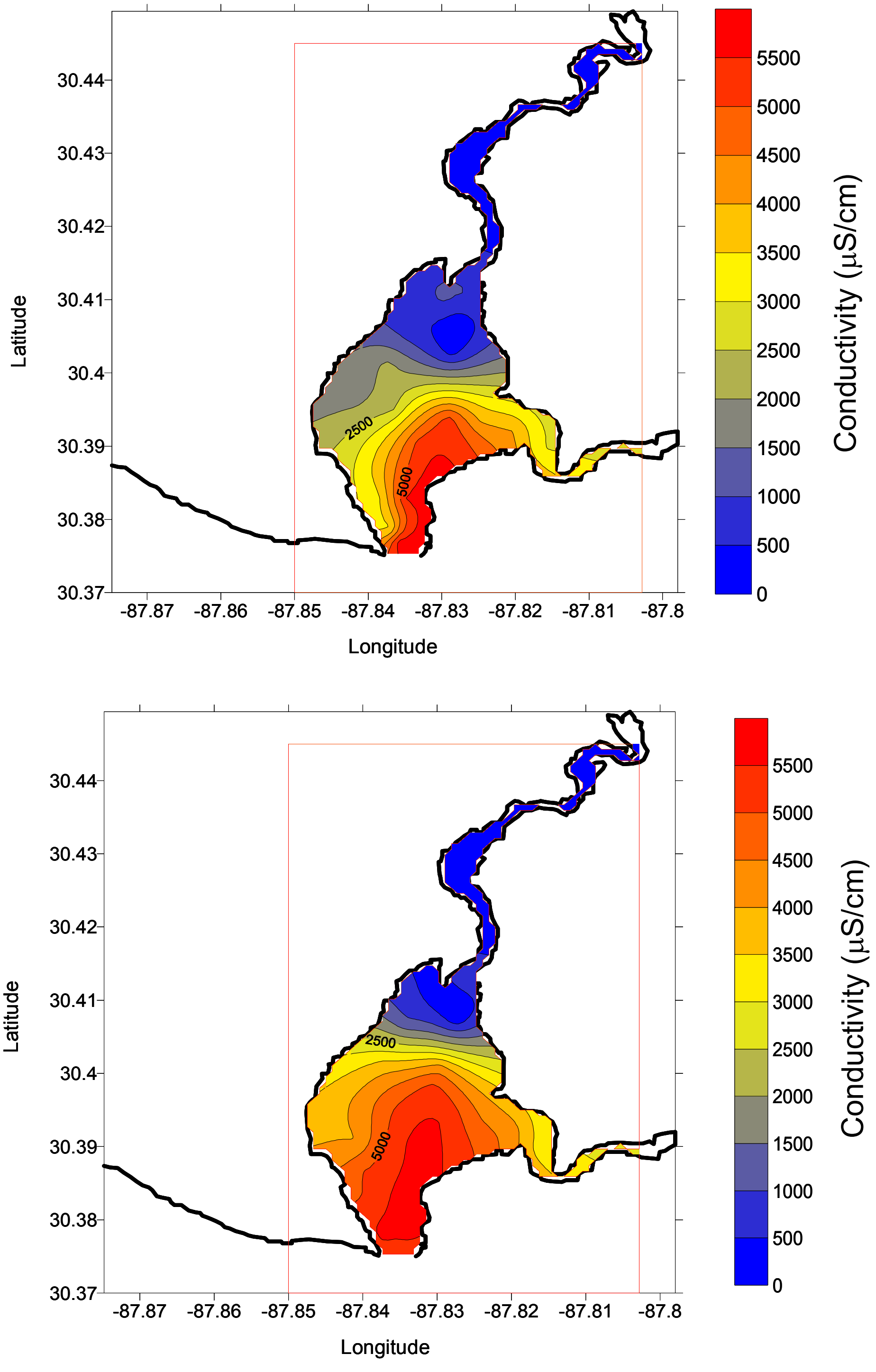

Figure 16. Contour map of surface (top) and 1-meter (bottom) conductivity levels in Weeks Bay. Similar to temperature and pH, higher conductivity readings can be found farther up the bay at 1-meter depth than those at the surface.

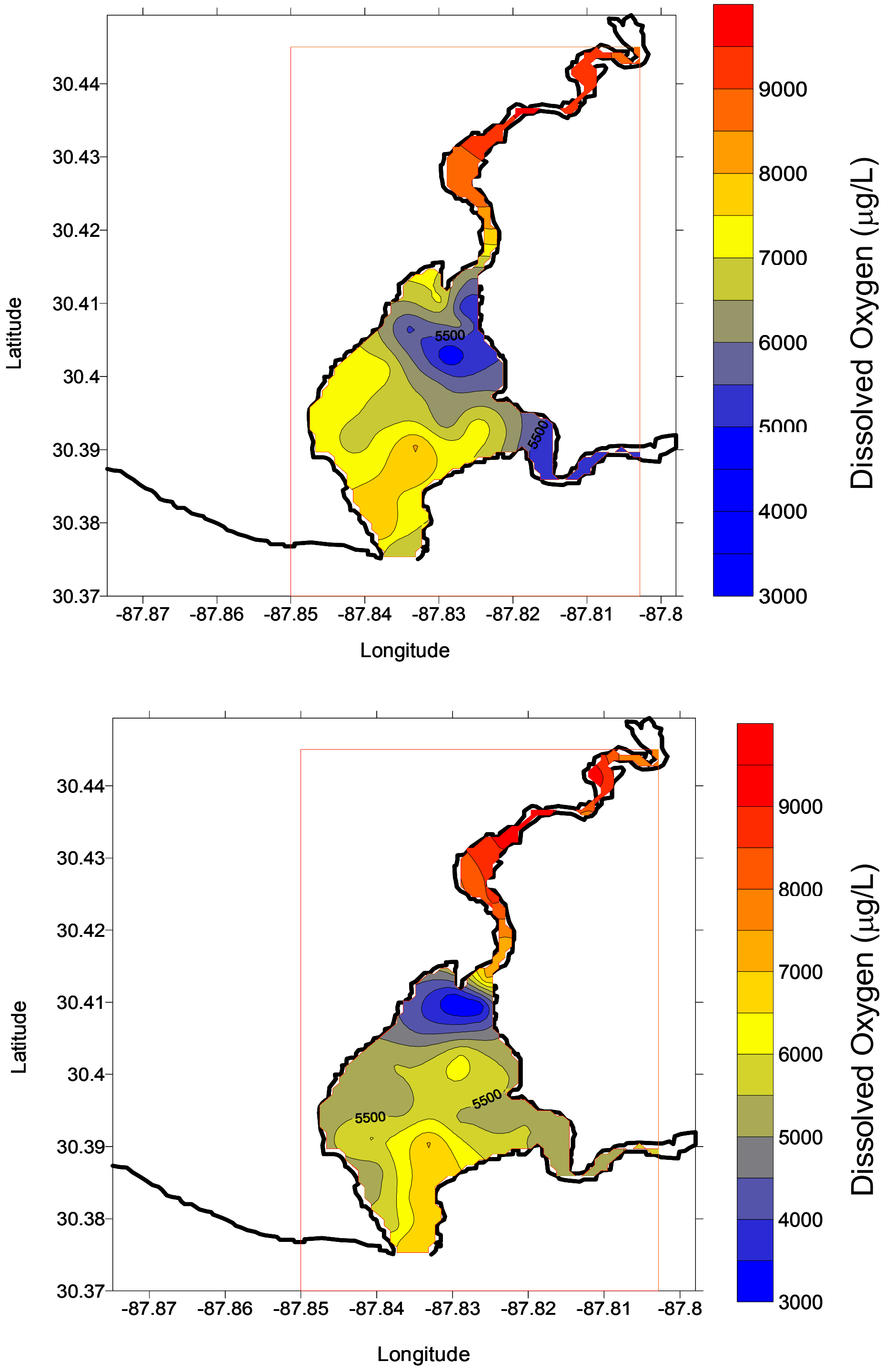

Figure 17. Contour map of surface (top) and 1-meter (bottom) DO levels. The lowest DO readings are located at the mouth of Fish River.

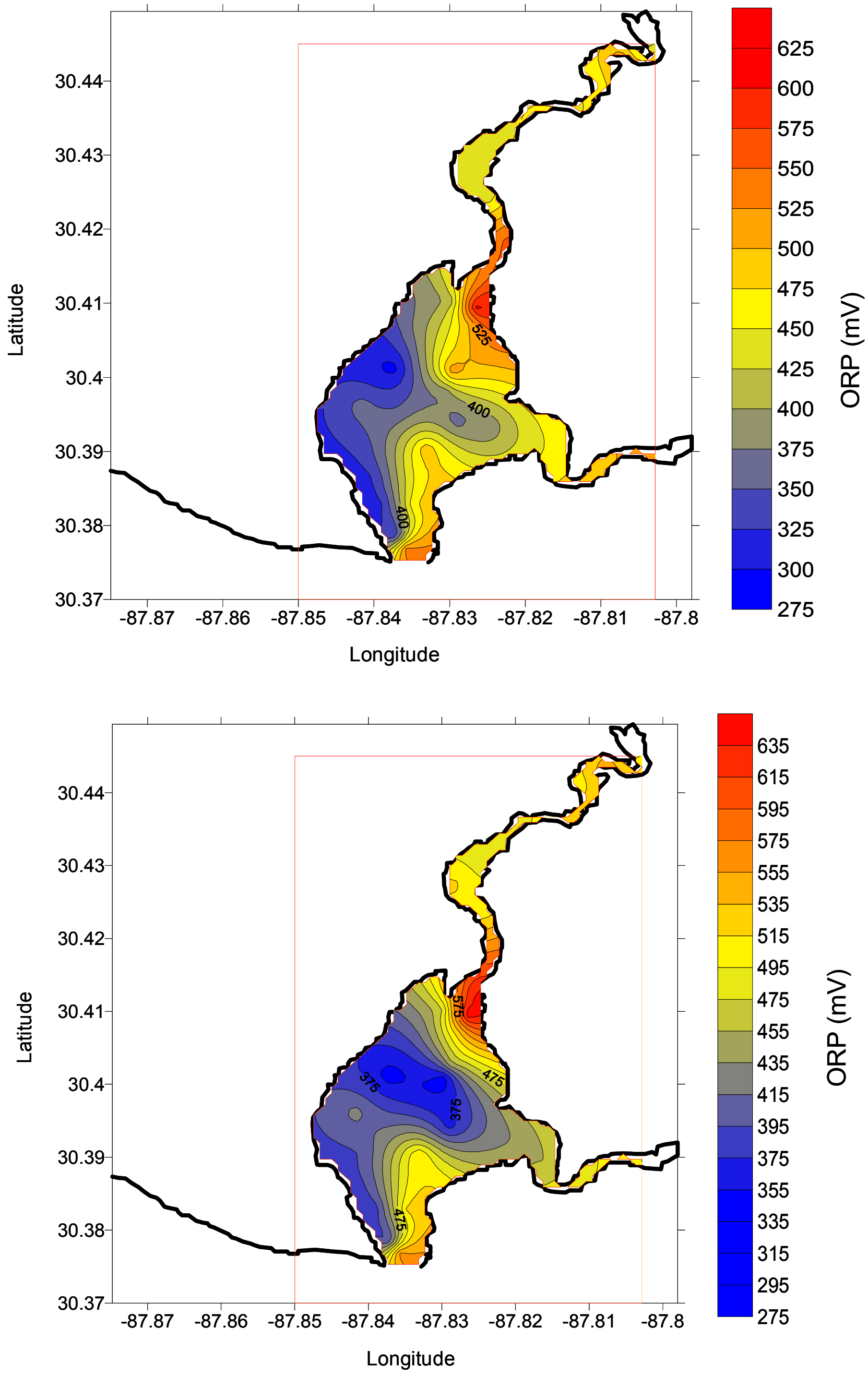

Figure 18. Contour map of surface (top) and 1 meter (bottom) ORP contour maps. Lowest ORP zones are found on the western side of the bay and the highest at the mouth of the Fish River.

same conditions can also increase the affinity of mercury to sulfides removing mercury from the system and reducing methylation (Kannan, 1998).

Along with field parameters chemical analysis of collected water samples were completed for major ions and trace elements. Data from major ion analyses are consistent with the results of the measured parameters. The surface water in the bay is predominated by an average Na/Cl molar ratio of about 0.86, similar to that of seawater. The surface water has lower SO_4/Cl ratios (average 0.048) with respect to that of seawater (~0.052), indicating that SO_4^{-2} may be removed by mineral precipitation (such as gypsum, $CaSO_4$) or bacterial sulfate reduction:

$$SO_4^{-2} + 2CH_2O + 3H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$$

Where CH_2O represents organic matter. Sulfate reduction is an important factor in Hg cycling as SRB take up Hg in its inorganic from and convert it to methylmercury through metabolic processes (King et al., 2002). This process may play an important role in the methylation of mercury in Weeks Bay. The surface water in the bay also has elevated metal content of Sr, Ni, and Rb, similar to that of seawater (Table 5). Cl/Br ratios of surface water, ranging from ~306 to ~318, are slightly higher than that of seawater (~288). Figure 19 shows the distribution of sampled waters using a piper diagram. The surface waters contain high amounts of Na and Cl, similar to values found in seawater. The groundwater analyzed contains high amounts of Na and HCO_3^-, indicating sodium bicarbonate type of groundwater. The Na-HCO_3 type high alkalinity of the groundwater

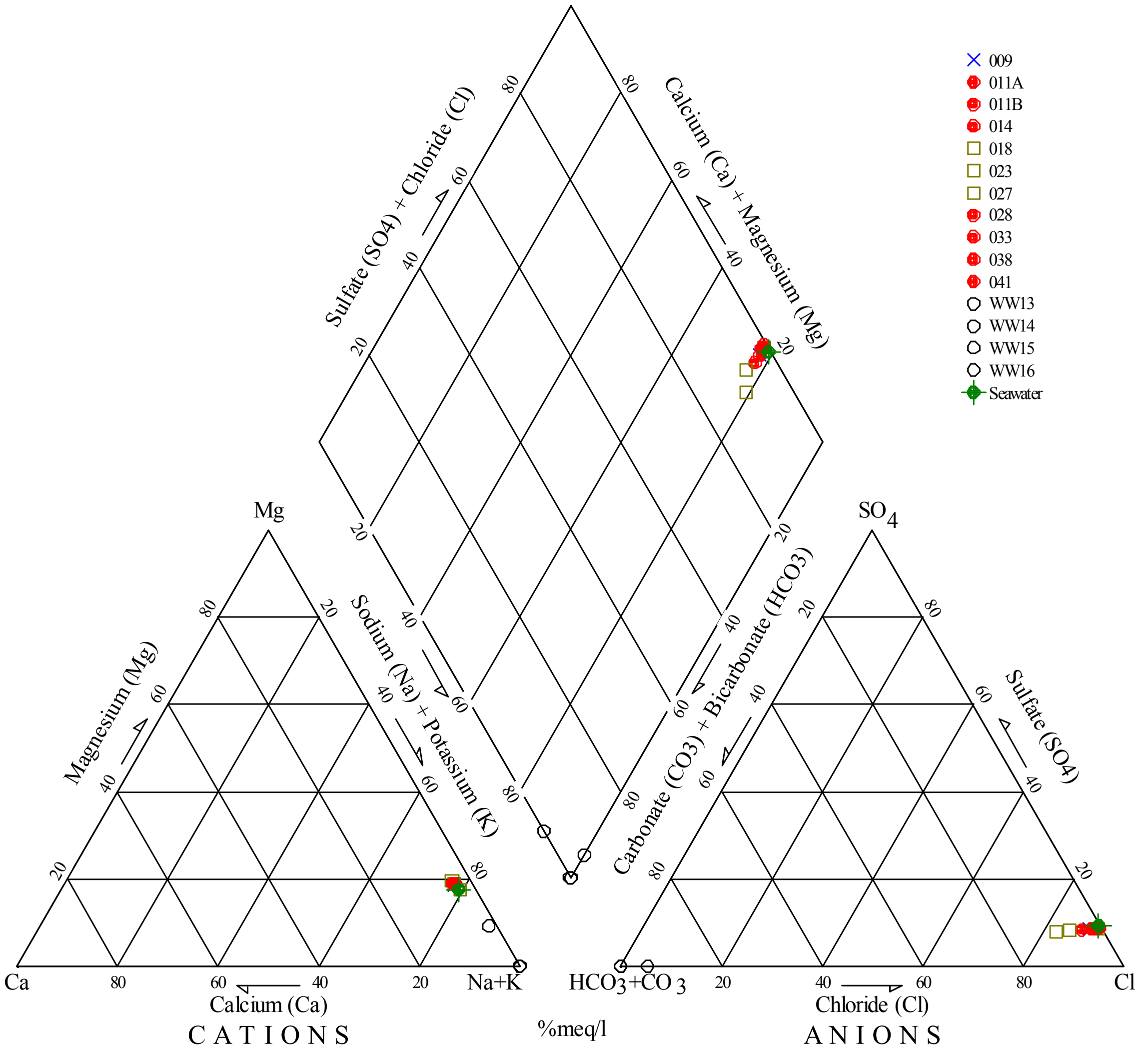

Figure 19. Piper diagram showing surface and groundwater compositions compared to that of seawater. Surface waters resemble those of seawater (i.e., Na-Cl types), whereas groundwater is sodium bicarbonate rich.

is most likely a result of the combination of dissolution of calcite and ion exchange (Marimuthu, 2005, Penny et al., 2005).

Chemical analyses of major ions also provide further information on the physical mixing and accompanying biogeochemical reactions. A graphic technique is used to evaluate mixing behavior (Figs. 20-23). In this method, chloride, a conservative (non-reacting) species, is plotted on the x-axis. The species of interest, which may or may not be conservative, is plotted on the y axis. The mixing behavior can be determined based on the proximity of data points to the straight line drawn between the seawater and freshwater end-members. Data points lying on or close to the conservative mixing line indicate that dissolved species exhibit conservative behavior. Non-conservative behavior is indicated if the data points deviate significantly from the conservative mixing line. Enrichment or depletion of species in solution may be caused by biogeochemical processes such as mineral dissolution/precipitation, ion-exchange, or microbial processes.

In all of the graphs, a linear trend reveals the conservative mixing between seawater and freshwater. River waters plotted near those of freshwater and bay waters, as influenced most by saltwater intrusion, has the highest major ions concentrations. The results of the graphical analyses indicate Na^+, Ca^{+2}, Mg^{+2} and Br^- exhibit conservative behavior during mixing. Only sulfate exhibits non-conservative depletion (about 10%). The reason for this depletion is unclear and may be a result of bacterial sulfate reduction.

Previous studies have found that some estuary environments show the highest levels of methylmercury in the upper portions near the mouths of tributaries. In the study area the upper estuaries contained low DO levels, low pH, and low salinity (Baeyens, 1998; Benoit, 1998; and Leermakers, 2001). These conditions are ideal for sulfate-

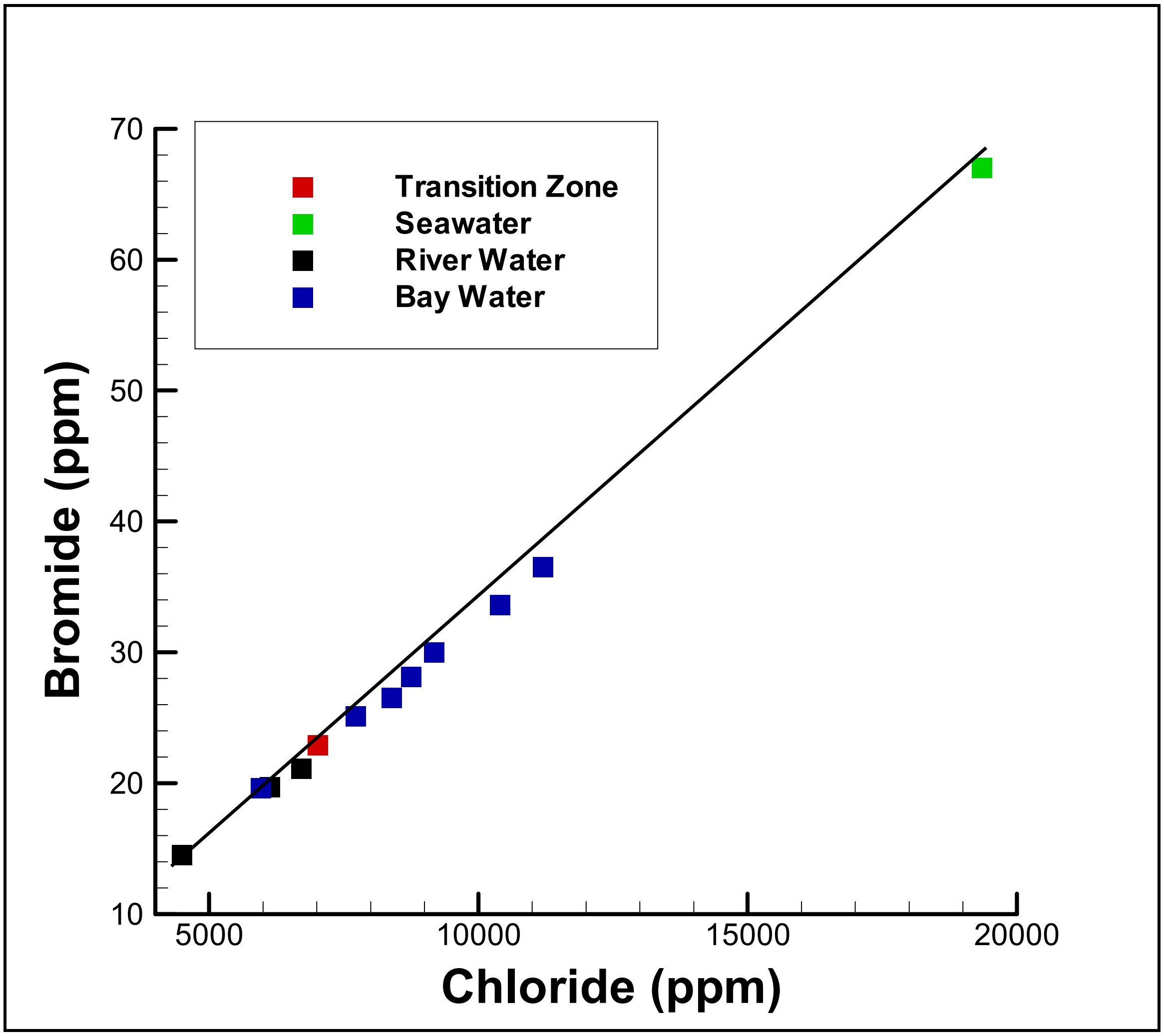

Figure 20. Plot of Cl versus Br. Linear pattern between various waters found within Weeks Bay.

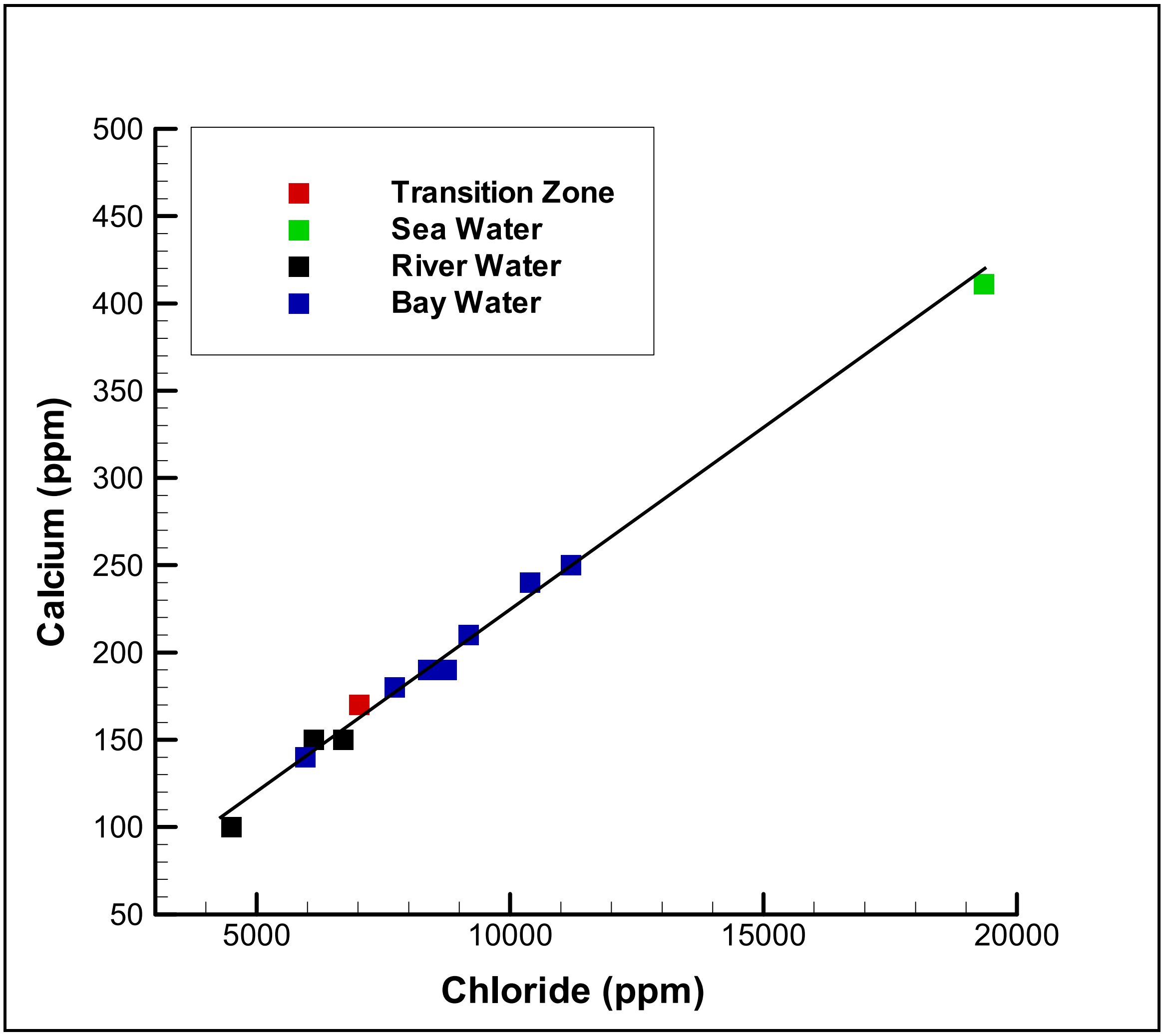

Figure 21. Plot of Cl versus Ca graph showing a similar linear pattern between waters.

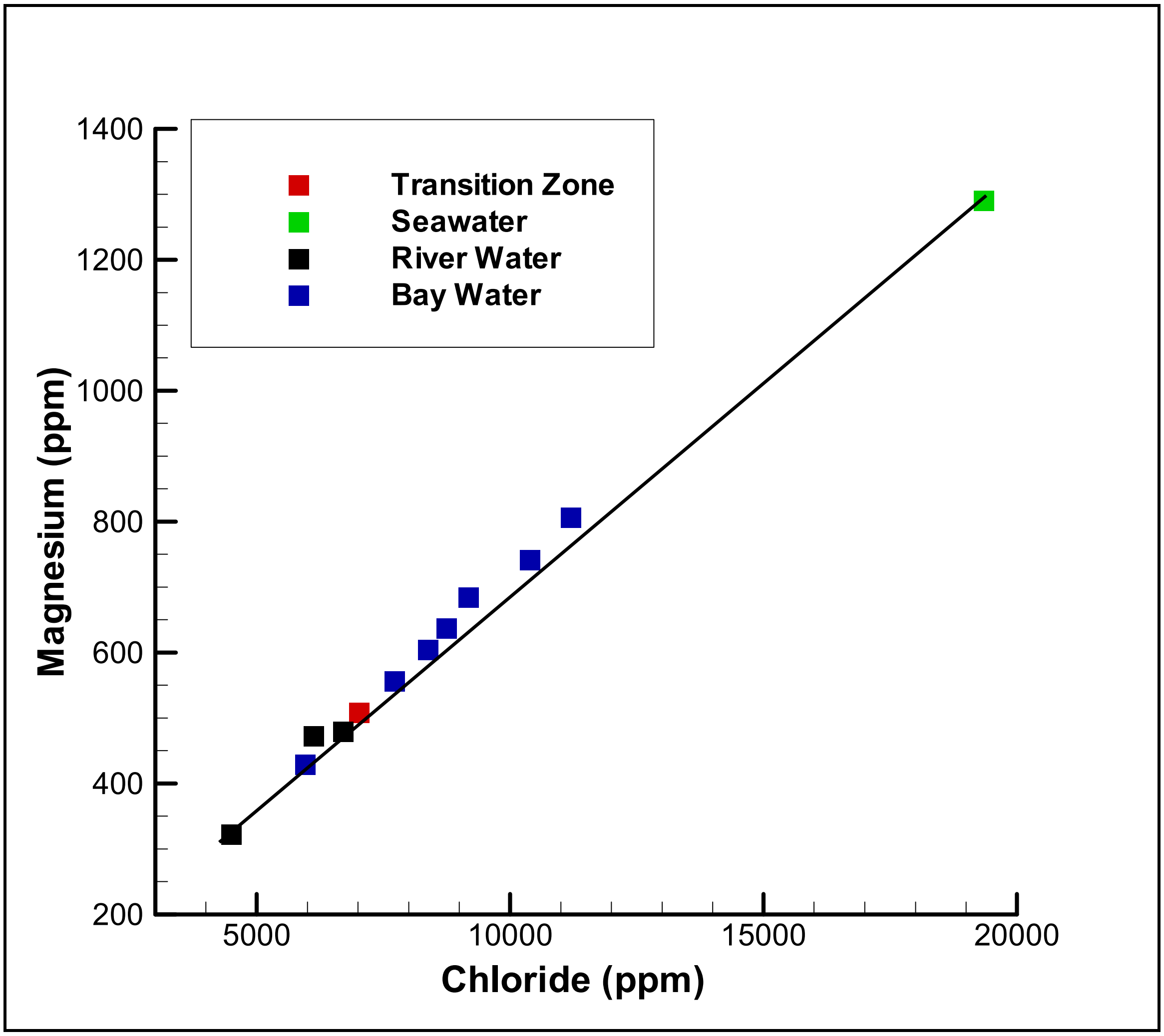

Figure 22. Plot of Cl versus Mg graph with a linear pattern between Weeks Bay watershed waters.

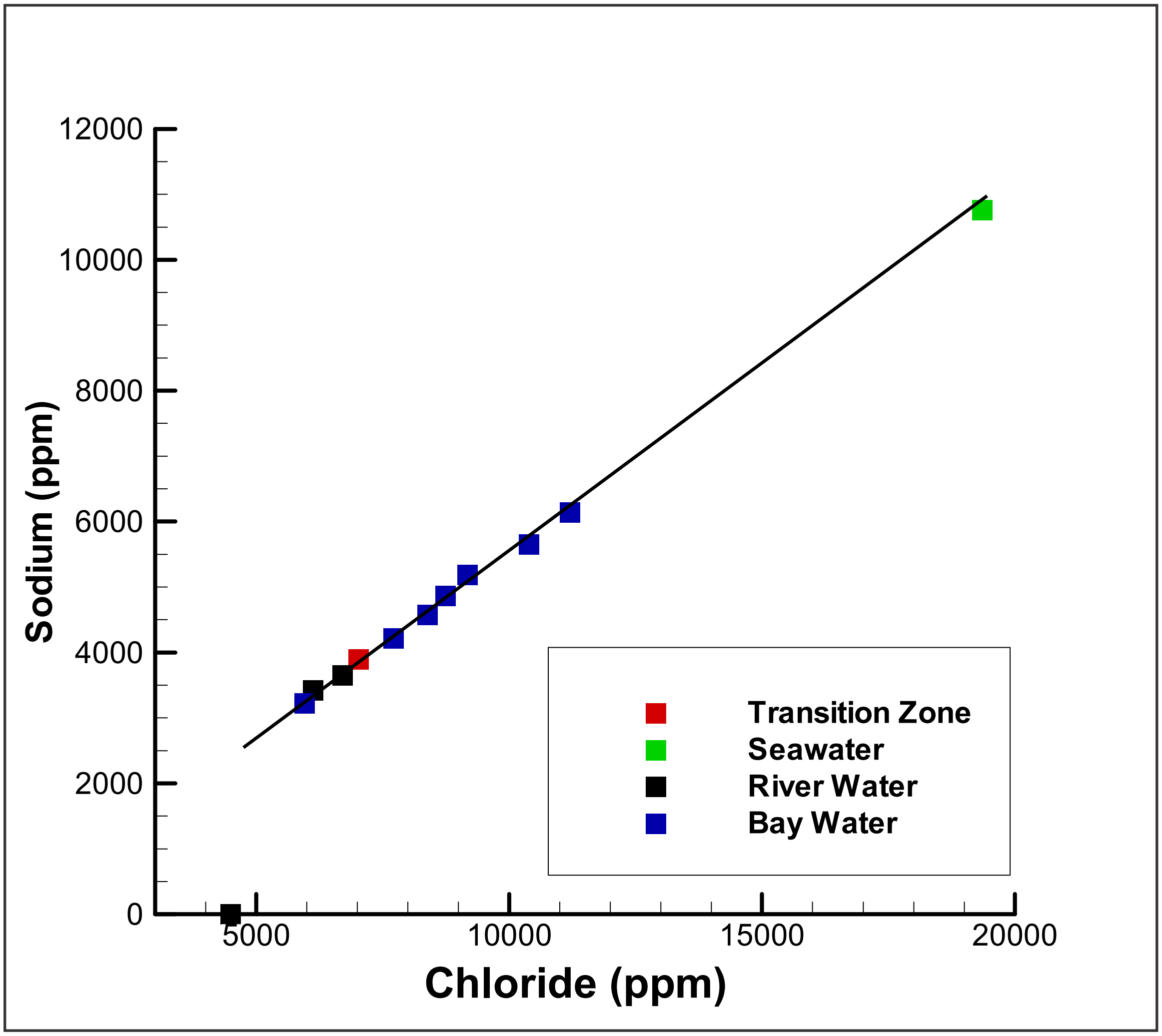

Figure 23. Plot of Cl versus Na graph showing mixing of waters within Weeks Bay with a linear pattern between waters.

reducing bacteria to exist which have been shown to play a part in the methylation of mercury (Benoit 2001, King 2002). These same conditions may exist within Weeks Bay at the mouth of the Fish River.

According to Drever (1997), DOC contents for rainwater range from 0.5 mg/L to 1.5 mg/L, seawater is about 0.5 mg/L, and river and lake waters range are 2 mg/L to 10mg/L. The DOC data collected from the surface waters range 1.4 mg/L to 2.2 mg/L. These results may indicate that the surface water of the bay and rivers are the result mostly rainwater of meteoric origin with some samples falling in the rivers and lakes range. However, these results may be skewed due to the mixing of lower DOC seawater and groundwater diluting the amount of DOC in the bay. The narrow range of DOC values indicate that DOC level is not an important factor in controlling the spatial distribution of Hg methylation in the Bay.

Groundwater Movement

Head levels of four clustered USGS monitoring wells on the western shore of Weeks Bay indicate that groundwater are discharging upward into Weeks Bay (Fig. 24). Head levels at WW13 and WW14, the farthest from the bay, are equal, suggesting horizontal groundwater movement. WW15 and WW16 are located closer to the bay and show a different groundwater flow pattern. WW16, slightly further inland from WW15, has head levels higher than those of WW13 and WW14, while the deeper well WW15, the closest to the bay, is an artesian well and has higher hydraulic head than the shallow WW16 in a nearby location. This suggests that groundwater is moving upward into Weeks Bay.

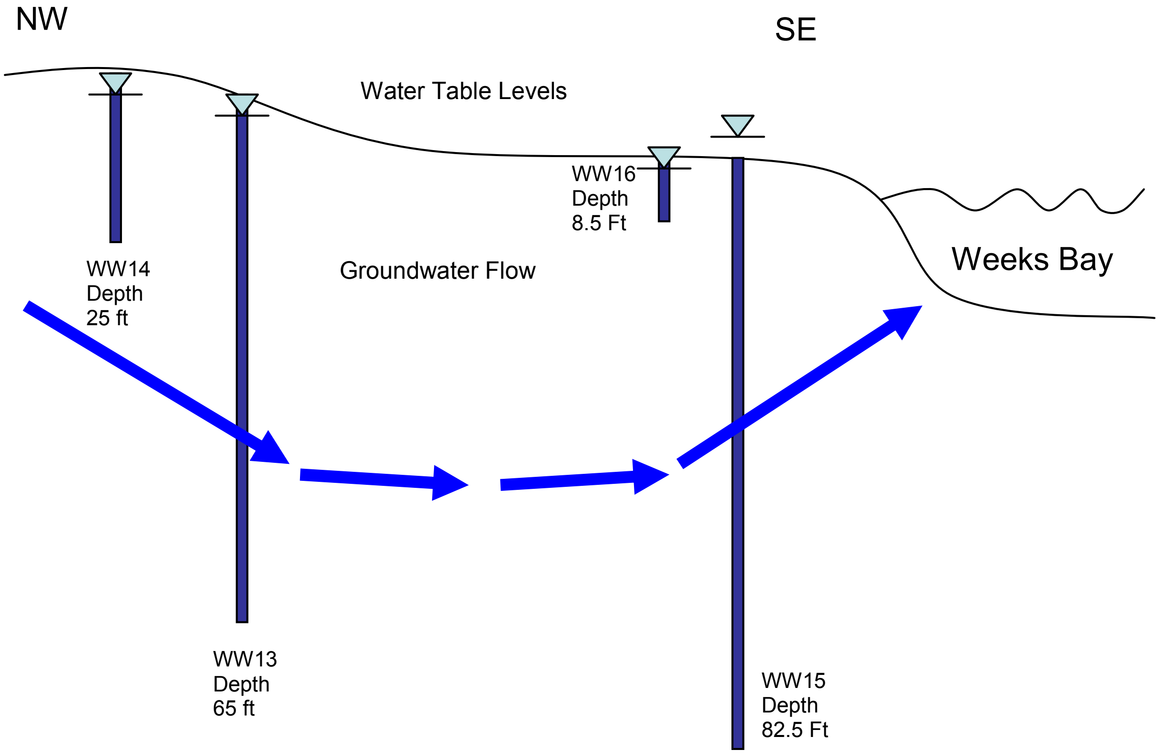

Figure 24. Diagnostic illustration of groundwater movement near the Week Bays. Deeper well WW 15 is an artesian well and has a higher hydraulic head than the adjacent shallow well WW16, indicating an upward movement of groundwater into Weeks Bay. Distance clustered wells WW 13 and 14 have the same hydraulic head, indicating horizontal flow predominates in the aquifer away from the bay.

Groundwater Influences

Data retrieved from USGS monitoring wells are different than that derived from surface waters. Three of these wells (WW13, WW14, and WW16) were found to contain mercury levels (6 – 8 ppb) higher than detection limits. The DOC in these wells ranges from 1.4 to 1.9 mg/L, with one well, WW15, reaching a value 3.3 mg/L. The DOC values of WW15 more closely resemble those of river and lake values, this may be the result of the surface water infiltration into the groundwater. This possibility is consistent with the higher conductivity found in WW15, which is similar to the conductivity of Weeks Bay (Table 5).

Stable isotope analyses provides more details about the mixing of waters and demonstrates the role that groundwater plays in influencing the chemistry of Weeks Bay surface water. Comparing oxygen and hydrogen isotopes of sampled sites along with seawater signature as well as the local meteoric water line sheds more lights on the nature of mixing and evaporation (Fig. 25). Again we can see the grouping of bay water, river water, and groundwater with the transition zone at the mouth of the Fish River between those of river water and bay water groupings. Groundwater isotope data values plot on or near the local meteoric water line (LMWL) (Cook, 1997; Penny et al., 2003), suggesting that groundwater has not undergone great evaporation or water rock interaction since its recharge. Water rock interaction is unlikely due to the increase in hydrogen to which water rock interactions would not contribute. In contrast, the Fish River waters are enriched in ^{18}O and ^{2}H and plot farther off the LMWL, indicating greater evaporation than groundwater. Bay water has the highest ^{18}O and ^{2}H values,

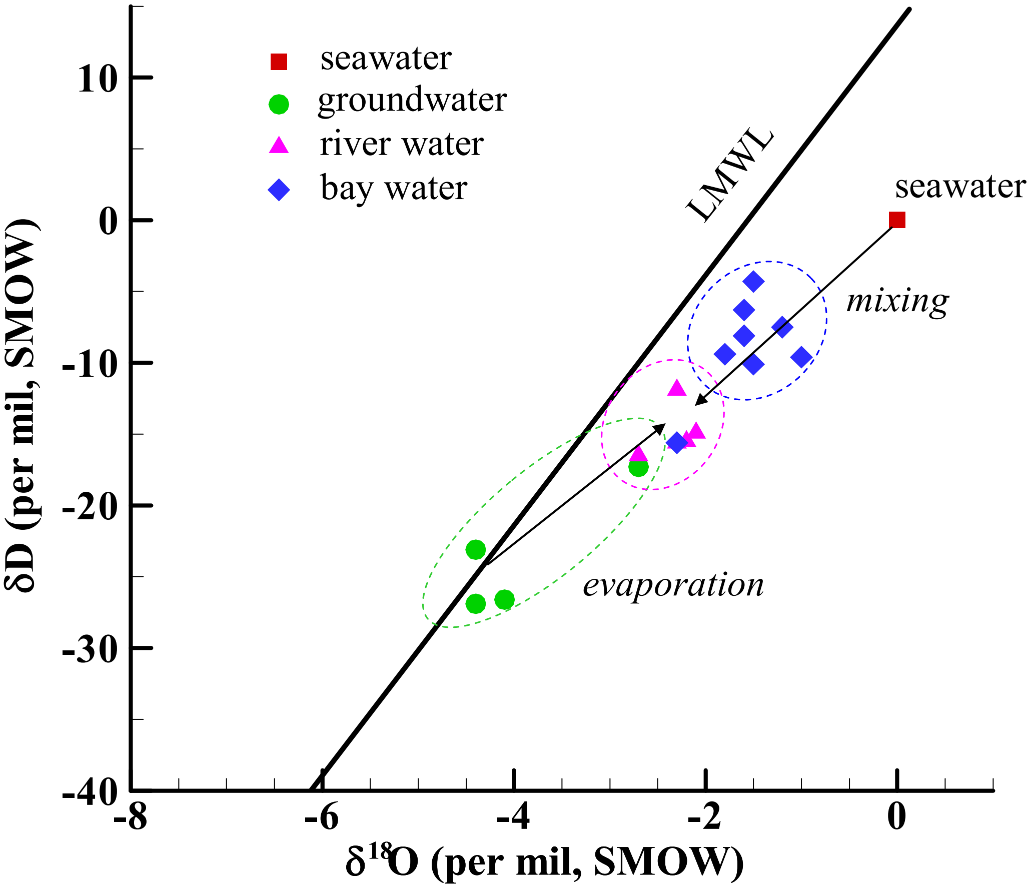

Figure 25. Plot of evaporation trajectory of local meteoric water line (LMWL) (Holser, 1979; Cook, 1997) and seawater mixing trend, shown using deuterium (δD) and oxygen ($\delta^{18}O$) isotope ratios of groundwater and surface water in Weeks Bay. As evaporation occurs in river waters, the waters become enriched in their isotopic signatures as evaporation preferentially removes lighter ^{16}O and ^{1}H. The data show that Fish River and Weeks Bay waters, which are farther off the LMWL, undergo greater evaporation than groundwater. The Weeks Bay water represents a mixture of two "end-member" waters: one of seawater and one of river water or groundwater of meteoric origin impacted by variations in evaporation rates.

indicating stronger influence from mixing with isotopically heavier seawater. The stable isotope signatures indicate that the Weeks Bay water represents a mixture of two “end-member” waters: one of seawater and one of river water or groundwater of meteoric origin impacted by various degrees of evaporation.

CONCLUSIONS

The most likely source for mercury contamination found in the Weeks Bay watershed is from atmospheric deposition. 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 Weeks Bay watershed.

The complex mixing that is taking place within the Weeks Bay watershed impacts the water chemistry and methylation of mercury. The addition of seawater, freshwater, and groundwater contribute to the conditions (e.g., warm, acidic, low-salinity) necessary for methylation. The oxygen and hydrogen isotope data suggest that the chemistry and quality of surface waters of river and bay are affected by evaporation, meteoric recharge, groundwater discharge, and mixing with seawater. The stable isotope signatures of groundwater fall close to the LMWL, indicating minimum evaporation prior to surface infiltration. River water and 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. Similar isotopic signatures and evaporation patterns are found in a coastal salt march in Australia (Marimuthu, 2005). 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 addition to physical mixing and evaporation, biochemical processes such as bacterial sulfate reduction may be at work in the watershed as indicated by non-conservative depletion of SO_4^{-2}. Bacterial sulfate reduction is known as the critical first strep for Hg methylation and bioaccumulation.

The intrusion of seawater into Weeks Bay creates a front of high salinity, high pH water that penetrates below low pH, low-conductivity freshwater. At this wedge interface, a depth difference of only a few centimeters causes rapid changes in water chemistry. Such salinity and thermal stratifications are pronounced in the bay at various seasons. The seasonal changes in salinity and thermal stratifications may control the location of mercury methylation and require further study. In addition, the discharge of acidic, low-salinity groundwater into the bay and river may contribute vital conditions that promote the methylation of mercury. The most rapid changes in water chemistry occur at the mouth of the Fish River leading into Weeks Bay. At this point, the mixing of several waters of different chemical characteristics creates a favorable environment (i.e., the presence of warm, acidic, and low-salinity waters) where methylation may occur and cause the spread of mercury contamination throughout the watershed via bioaccumulation. Low DO and ORP values observed in this mixing zone suggest active microbial processes that are an important factor in initializing Hg methylation.

Seasonal variations also allow for increased and decreased methylation rates in the watershed. Similar variations also are seen in other mercury contaminated estuary environments (Benoit, 1998; Mason, 1999; Leermakers, 2001; Conaway, 2003). Summer conditions are characterized by relatively high temperature, lower pH, low conductivity, low DO and high ORP. Summer months are also the wet test season for the region as indicated by the data of mercury deposition and precipitation. The bay chemistries during winter and spring times were characterized by low temperatures, high pH, low conductivity, high DO, and low ORP. The spring and winter data appears to have more uniform conditions throughout the bay, indicating greater mixing and less stratification. This could be a result of increased winds and less stream discharge as a result of reduced precipitation.

Comparing observed conditions to those of similar estuaries in North America, generalizations can be made of when and where mercury methylation may occur within Weeks Bay. In the Chesapeake Bay, Scheldt Estuary, and San Francisco Bay mercury concentrations are highest during high water flow seasons. During these seasons all of these estuaries exhibited high temperatures, low pH, low conductivity, and low DO (Benoit, 1998; Mason, 1999; Leermakers, 2001; Conaway, 2003). These conditions are similar to those found in Weeks Bay and indicate that the greatest methylation is occurring during summer months.

Additional studies of methylmercury within the Weeks Bay watershed are needed to understand more precisely the complex physical, chemical, and biological influences. Further study of Weeks Bay tributaries is needed to gain more information on how river and groundwater sources may be influencing the Weeks Bay. Also, water chemistries in and around the transition zone at the mouth of the Fish River need to be studied more fully to see if that is the area where the maximum methylation of mercury is occurring. These studies can be completed with analyzing sediment and water samples for mercury and methylmercury. Studies involving biological activities and microbial composition can also be completed to further our knowledge of methylation within Weeks Bay. The comparisons among microorganisms, contaminated fish findings and water chemistry can be analyzed for correlations that may reveal locations of methylation.

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