MONOMETHYLMERCURY CONCENTRATIONS ON THE EASTERN TEXAS-LOUISIANA SHELF DURING THE FORMATION, PEAK, AND DISAPPEARANCE OF HYPOXIA

A Thesis

by

SARA ELIZABETH KEACH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2006

Major Subject: Oceanography

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Approved by:

Committee Co-Chairs,	Gary Gill
	Peter Santschi
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	Jay Rooker
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ABSTRACT

Monomethylmercury Concentrations on the Eastern Texas-Louisiana Shelf
During the Formation, Peak, and Disappearance of Hypoxia. (May 2006)
Sara Elizabeth Keach, B.S. Roger Williams University
Co-Chairs of Advisory Committee: Dr. Gary Gill
Dr. Peter Santschi

A study of monomethylmercury (MMHg) concentrations in the water and sediment of the hypoxic zone in the northeastern Gulf of Mexico was conducted on several cruises between April 2004 and May 2005. Surface water MMHg concentrations were low and constant throughout the sampling period. Bottom water concentrations displayed a seasonal trend: maximum MMHg concentrations were in June/July 2004, decreased to a minimum in October 2004, and in May 2005 concentrations had begun to increase. MMHg concentrations and MMHg as a percent of THg in surface sediment (0-2 cm) also followed this trend. Bottom water dissolved oxygen and temperature displayed inverse relationships with bottom water MMHg concentrations. This correlation between dissolved oxygen and MMHg is typical for low-oxygen waters, but the relationship between temperature and MMHg is relatively unique. A possible explanation is that warmer summer temperatures inhibited bacterial methylation. Stratification intensity (quantified as N^2) was strongly correlated with bottom water MMHg concentrations, indicating either increased methylation at the pycnocline or that the pycnocline inhibited vertical mixing, thus limiting MMHg to the bottom water. Benthic flux estimations indicate that sediment release of MMHg could be a significant source of MMHg to bottom water. The presence of an oxygenated layer in the surface sediment could have played a role in inhibiting MMHg flux during oxic conditions; a decrease in the thickness of this layer under hypoxic conditions likely allowed MMHg to diffuse into the bottom water. Dissolved oxygen seemed to play an important role in controlling sediment MMHg concentrations with highest methylation rates in sediment under hypoxic water. Overall, sites closest to the Mississippi River mouth displayed the

highest MMHg concentrations. Further research will need to be done in this area to fully characterize the relationship between biogeochemical parameters and MMHg concentrations.

DEDICATION

This is dedicated to my parents, who have always encouraged me to follow my dreams – even if it means following them to Texas. Also, this thesis is dedicated to Carlton, whose love and support have helped me in so many ways. I wouldn't be where I am today without you all.

ACKNOWLEDGEMENTS

I would like to thank Dr. Gary Gill for his guidance throughout my graduate education. I am grateful for his encouragement, financial support, and helpful comments. Also, thanks to Dr. Steve DiMarco for a chance to work aboard the MCH cruises, and for accommodating my sampling needs. I am also grateful to Dr. Peter Santschi and Dr. Jay Rooker for all their time and support.

Thanks to everyone in the LOER mercury lab. Thanks especially to Ron Lehman who coached me through my analytical troubles, and made working in the lab every day an enjoyable experience. Thanks also to Dr. Key-Young Choe, who patiently taught me everything I needed to know about methylmercury analysis.

This research was supported by Dr. Gill's CALFed grant. Ship time was possible due to Dr. DiMarco's NOAA funding.

A special thanks to my friends in College Station and in Galveston – especially those who helped me collect my samples.

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INTRODUCTION

Most of our knowledge of mercury in aquatic systems comes from terrestrial freshwater sources; comparatively little is known about marine systems even though human exposure to monomethylmercury (MMHg) is primarily through the consumption of marine fish and shellfish. Although all mercury species can be harmful to humans and other organisms (Goyer and Clarkson, 2001), MMHg is of chief concern because it bioaccumulates and is a neurotoxin (Clarkson, 1997). At high concentrations MMHg can cause brain damage and loss of motor skills in adults while more serious effects have been documented in children and fetuses (Clarkson, 1997; Borum et al., 2001). Environmental and health agencies have increased public awareness of mercury poisoning, but complete knowledge of Hg cycling and MMHg formation in aquatic systems is needed to fully understand this problem (Mason and Benoit, 2003; National Science and Technology Council, 2004).

Mercury is a metal that is ubiquitous in the environment and is found at picomolar concentrations in pristine aquatic systems (Wiener et al., 2003). It is released to the atmosphere through natural - volcanic emissions, soil degassing, and volatilization - and anthropogenic – fossil fuel burning, smelting, and waste incineration - processes. Mercury cycles through the atmosphere primarily as elemental mercury (Hg^o) and can form Hg(II) via photooxidation or biologically mediated reactions. It is then deposited into terrestrial and aquatic environments (Lin and Pehkonen, 1999; Mason and Benoit, 2003). A portion of this Hg(II) will be reduced back to Hg^o and vaporized into the atmosphere, while the rest will remain in the environment. A fraction of Hg(II) remaining in aquatic systems will be methylated, creating MMHg (Fitzgerald and Mason, 1997).

This thesis follows the style of *Marine Chemistry*.

A majority of MMHg formation in aquatic environments is microbially produced (Gilmour and Henry, 1991; Choi et al., 1994), although some is produced photochemically (Hamasaki et al., 1995) or through complexation with humic compounds (Nagase et al., 1984). Methylation can occur in sediment as well as in the water column (Mason et al., 1993; Watras and Bloom, 1994;), but typically higher methylation rates are found in sediment (Compeau and Bartha, 1985; Gilmour et al., 1998) where microbes are more abundant (Wiener et al., 2003). Although methylation is high in sediment there are still many bacteria in the water; methylation in the marine water column should also be considered an important source of MMHg since its volume is large enough to create a significant amount of MMHg (Gilmour and Henry, 1991).

Mercury is absorbed into bacteria and microalgae via passive diffusion (Mason et al., 1996), accumulating to over 1,000 times the concentration in the surrounding environment (Boudou and Ribeyre, 1997). Based on our knowledge of methylation by the bacterium *Desulfovibrio desulfuricans* LS, it is an enzymatically catalyzed process in which a reactive methyl group is transferred to the absorbed Hg (Choi et al., 1994; Benoit et al., 2003). Since this is a natural process, methylating bacteria have developed a resistance to the effects of MMHg accumulation (Barkay et al., 2003). Once MMHg is absorbed into bacteria, it is able to bioaccumulate up the aquatic food chain (Boudou and Ribeyre, 1997). This ability is attributed to the lipophilic character of MMHg as it easily binds to fatty tissues (Mason et al., 1996; Clarkson, 1997). MMHg concentrations increase with increasing trophic level, the highest concentrations – typically 10^6 times the levels in surrounding waters - being found in large fish and marine mammals.

Although MMHg is produced by bacteria, methylation rates vary greatly with many environmental parameters. Dissolved oxygen (DO), sulfide/sulfate concentrations, organic matter (OM) concentration and composition, pH, salinity, light intensity, and temperature all directly or indirectly affect Hg(II) methylation. MMHg production seems to be highest in anoxic, high sulfate/low sulfide, slightly acidic, low salinity, warm, organic-rich environments (Wiener et al., 2003). Since MMHg concentrations have been correlated with *in situ* MMHg production (Gilmour et al., 1998), concentrations and information about relevant environmental parameters will provide a great deal of information about MMHg production in a given environment.

Environmental Parameters Controlling Methylation

Dissolved Oxygen

It is well established that MMHg production is highest in anoxic and hypoxic (DO <1.4 mL/L) environments (e.g. Compeau and Bartha, 1984; Bloom et al., 1991; Mason et al., 1999; Ullrich et al., 2001) where Hg methylation is high and demethylation is minimal (Gilmour and Henry, 1991; Fitzgerald and Mason, 1997). Increased methylation under low oxygen conditions has been attributed to the increased abundance and activity of sulfate reducing bacteria (SRB) (Benoit et al., 1999; King et al., 2001). SRB thrive in anoxic environments and have been identified as principal mercury methylators in marine ecosystems (Compeau and Bartha, 1985; Pak and Bartha, 1998; King et al., 2001).

In low oxygen conditions, methylation is often higher in the sediment than in the overlying water (Wiener et al., 2003). Several studies have shown that oxygenated surface sediments – even a thin layer – can act as a barrier against MMHg diffusion from sediments into the water column (Gagnon et al., 1996). When surface sediment becomes anoxic, the oxygenated barrier disappears and MMHg can be released from the sediments (Mason and Lawrence, 1999), increasing concentrations in the bottom water (Bloom et al., 1999; Gill et al., 1999; Mason et al., 1999).

Sulfate/Sulfide

As dissolved oxygen is removed from the water column and sediment, bacteria move down the chain of electron acceptors, eventually using sulfate as an energy source. MMHg production is correlated with sulfate and sulfide concentrations (Benoit et al., 1999) due to the production of MMHg by SRB. The presence of sulfate enhances SRB activity, therefore increasing methylation rates (King et al., 2001). Sulfide is a byproduct of sulfate reduction and at low concentrations sulfide has been shown to stimulate MMHg formation by producing neutrally charged HgS^{o} which can diffuse across bacterial membranes (Benoit et al., 1999). Once in the bacteria, Hg can be converted to MMHg. At higher concentrations, sulfide inhibits MMHg formation by producing charged mercury/sulfide complexes such as HgS_2^{2-} and $HgSOH^{-}$ that are not bioavailable (Jay et al., 2000). Sulfate is non-limiting in marine environments and the sulfide produced often reaches concentrations high enough to inhibit bacterial methylation. This is more likely to occur in sediment because water is more easily mixed allowing fresh sulfate pools can be made available (Eckley and Hintelmann, 2005) and high sulfide concentrations to disperse.

pH

It has been suggested that changes in pH affect MMHg production by influencing mercury and sulfide speciation (Benoit et al., 2003). Since HgS^{o} and other uncharged Hg-S complexes are the mercury species that most easily diffuses across bacterial membranes (Benoit et al., 2003), a decrease in these species would result in lower methylation rates. There is also evidence suggesting that low pH promotes the release of metals from sediment (Duarte et al., 1991; Ullrich et al., 2001), resulting in increased MMHg concentrations in bottom water. Due to changes in speciation and increased fluxes, most studies agree that pH is inversely correlated with MMHg concentration in the water column (Ullrich et al., 2001; Boszke et al., 2003). In marine environments, pH is stable and is rarely a factor that stimulates changes in MMHg concentration.

Light Intensity/ Photosynthetically Active Radiation (PAR)

Light levels have been suggested to control MMHg production by influencing redox conditions at the oxic/anoxic interface (Gill et al., 1999). Krabbenhoft et al. (1998) noticed diel variations in MMHg concentrations during sampling in the Florida Everglades. They reported a net accumulation of MMHg at night, and a decrease in production during daylight hours (Krabbenhoft et al., 1998). Gill et al. (1999) explained this by suggesting that photosynthesis increased oxygen concentrations in the benthos during the day, therefore limiting the activity of SRB. It is likely that light penetrates to the sediment surface in shallower areas of the Gulf of Mexico, so differences in light intensity could affect MMHg concentrations.

Salinity

Blum and Bartha (1980) reported an inverse correlation between MMHg concentration and salinity. Their observation is supported by comparing typical MMHg concentrations in unpolluted freshwater lakes (~25 pM; Ullrich et al., 2001) to typical open ocean values (0.6 ± 0.6 pM; Fitzgerald and Mason, 1997). In freshwater, dominant mercury species include $Hg(OH)_2$, HgOHCl, and $HgCl_2$, all of which are uncharged and could diffuse across bacterial membranes. Salinity may directly inhibit methylation rates by forming charged mercuric chloride compounds (e.g. $HgCl_3^-$ and $HgCl_4^{2-}$) that cannot diffuse across bacterial membranes (Barkay et al., 1997) and are therefore unavailable for methylation.

Temperature

Increases in temperature enhance microbial activity resulting in an increase in MMHg production by SRB. Methylation rates may have a seasonal trend, becoming elevated during the warmer -late spring and summer - months (e.g. Hintleman and Wilken, 1995; Watras et al., 1995; Choe and Gill, 2003). Korthals and Winfrey (1987) found that changes in temperature accounted for roughly 30% of these seasonal MMHg variations. MMHg fluxes from the sediment also displays a seasonal trend that can be correlated with temperature; typically increases in temperature stimulate increased benthic flux (Wright and Hamilton, 1982; Gill et al., 1999; Choe and Gill, 2003).

Organic Matter

Organic matter (OM) is a food source for bacteria so its presence promotes microbial growth and activity. This is confirmed by indirect evidence suggesting that OM impacts sulfur concentration, an indication of SRB activity (Mason and Lawrence, 1999). By increasing bacterial activity, OM also increases MMHg production, especially in sediment (Gagnon et al., 1996; Benoit et al., 2003).

OM also appears to have a role in controlling MMHg mobility (Boszke et al., 2003) and bioaccumulation (Mason and Lawrence, 1999). MMHg has a strong affinity for OM, especially fulvic and humic acids; many studies report a strong correlation between OM and MMHg concentrations (Leermakers et al., 2001; Boszke et al., 2003). Boszke et al., (2003) proposed that OM induces the release of Hg from Hg-S complexes by binding the Hg in soluble Hg –DOM complexes. This is supported by Mason and Lawrence (1999) who found an inverse relationship between organic content and the bioavailability of MMHg in both sediments and the water column. Hg-DOM complexes likely dominate over inorganic-Hg complexes in coastal and estuarine environments (Fitzgerald and Mason, 1997; Han et al., 2006).

The degree that each of the above environmental parameters control MMHg concentrations and fluxes in the sediment and water column varies greatly, and many of these trends do not hold true in all aquatic environments (Ullrich et al., 2001). Most of these parameters are interrelated, making it difficult to attribute increased methylation to a single variable. Although this thesis does not investigate all the above mentioned parameters, it does relate MMHg concentrations to some of the controlling factors in the water column and sediments of the Gulf of Mexico hypoxic zone. This investigation of MMHg in a unique system like the Gulf of Mexico will add to the limited literature and expand our understanding of the factors controlling the mercury methylation process in marine systems.

Site Description

The Mississippi and Atchafalaya River outflows are dominant features in the northern Gulf of Mexico. Each year the two rivers discharge freshwater at an average rate of 14,000 m^3/s into the northern Gulf of Mexico (Rabalais et al., 2001); this makes the Mississippi discharge the sixth largest freshwater output in the world (Wiseman et al., 1997). The Army Corps of Engineers has controlled the river flows, allowing 67% of their combined output to flow west over what becomes the hypoxic zone (Rabalais and Turner, 2001). Highest discharge rates are typically in the spring (March – April), with large interannual variability.

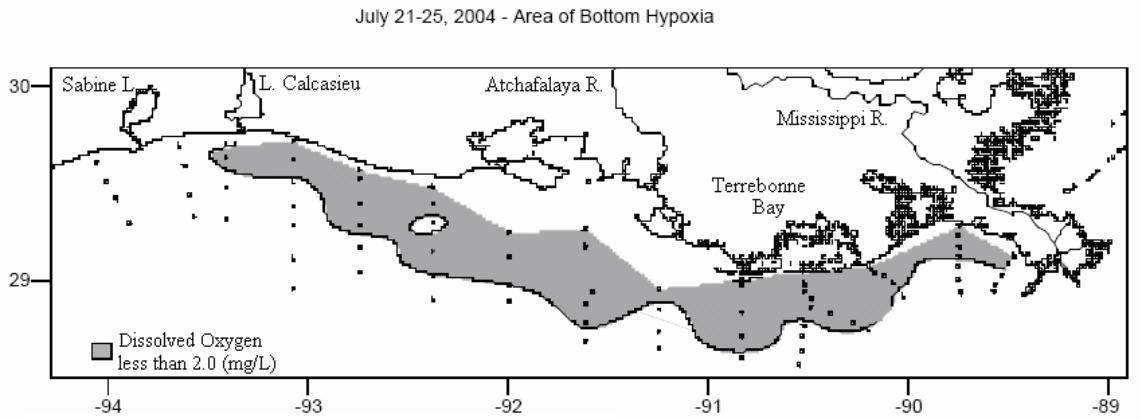
In early spring, as river flow increases, winds and storms are normally strong enough to mix the water column. During late spring and early summer these winds decrease, leaving the freshwater to stratify the Northern Gulf (Rabalais et al., 2002). Stratification in the Gulf is primarily based on salinity differences resulting from increased freshwater discharge dropping surface salinities over the hypoxic zone. The pycnocline also strengthens as surface waters warm over the summer.

Rabalais and Turner (2001) have determined there is roughly a two month lag time between increased Mississippi River flow near the mouth of the river (at Tarbert Landing) and the onset of hypoxia. In most years, this means oxygen concentrations begin to drop in May and last through September when increased extratropical cyclones mix the shelf waters (Rabalais et al., 1994; Nowlin et al., 1998).

The size of the hypoxic area varies yearly, but is known as the third largest hypoxic zone in the world (Rabalais et al., 2002) and normally extends from the mouth of the Mississippi River to the Texas border. During the peak of hypoxia in July 2004, the Dead Zone measured 15,040 km^2, in 2005 its area was 11,840 km^2 (LUMCON, 2004; LUMCON 2005; Fig. 1).

Mercury in the Gulf of Mexico

Little is known about Hg or MMHg in the Gulf of Mexico (National Science and Technology Council, 2004), but other low oxygen, marine systems have been studied and have shown above average MMHg concentrations (e.g. Pettaquamscutt estuary, Mason et al., 1993; Gulf of Trieste, Covelli et al., 1999).



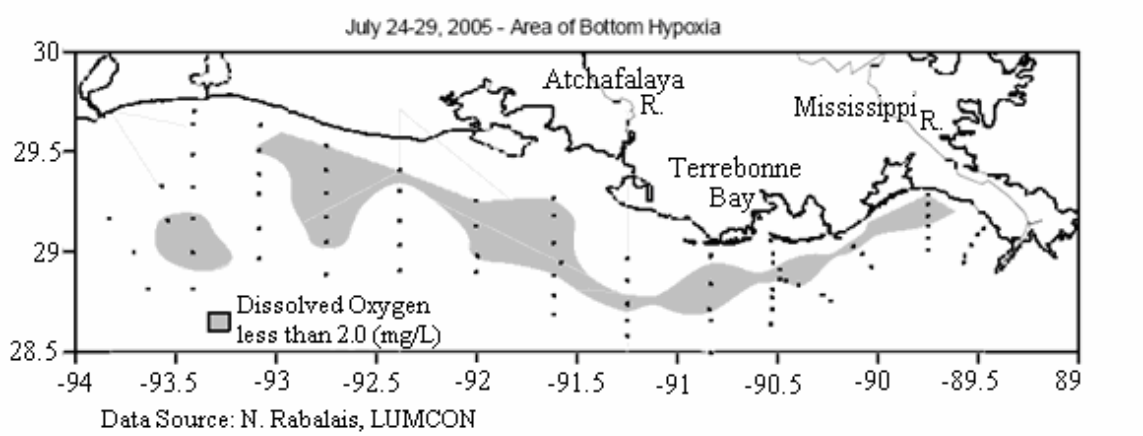


Fig. 1. Area of bottom water hypoxia at the peak of hypoxia in 2004 and 2005 (LUMCON: 2004, 2005).

Two studies conducted in the Gulf of Mexico have measured Hg concentrations in benthic invertebrates. Neff (2002) found Hg concentrations in Gulf oysters range from 0.007 - 0.05 ppm (wet weight), and concentrations in blue crabs range from 0.05 - 0.08 ppm (wet weight). Ache (2000) reported that American oysters in the Gulf have an average Hg concentration between 0.05 – 0.20 ppm while blue crabs have Hg concentrations of 0.21 – 0.30 ppm (wet weight). Although none of these concentrations are dangerously high, they are elevated with respect to background concentrations and suggest that MMHg is entering the food web.

Elevated MMHg concentrations in benthic invertebrates – especially filter and deposit feeders – have been reported in other environments and has been strongly correlated to MMHg concentrations in surface sediment (Mason and Lawrence, 1999). This correlation suggests that bioavailable MMHg is present in the surface sediment of the Gulf of Mexico and is being incorporated into the food chain.

This Hg is carried through trophic levels of the food web, and is most pronounced in Gulf of Mexico fish. Some fish in the Gulf of Mexico contain MMHg concentrations in their tissues that exceed the EPA's recommended consumption level of 0.3 ppm (Borum et al., 2001) and fish consumption advisories for king mackerel and some other larger species are in effect for all Gulf States (Ache et al., 2000). Ache et al. (2000) recorded average MMHg concentrations in Gulf of Mexico pelagic king mackerel to be 1.05 ppm (ww); this is higher than concentrations in estuarine king mackerel of the same size, indicating that MMHg is a part of the Gulf of Mexico food web, and not necessarily present in the local estuaries.

Elevated Hg concentrations in these Gulf species suggest MMHg is present in their environment (Gilmour et al., 1998). There are three unique characteristics of the Gulf of Mexico that could be a possible source for increased MMHg production: contamination from the Mississippi and Atchafayala Rivers, the large number of oil platforms, and the seasonal hypoxia that develops in the Northern Gulf. Garbarino et al. (1995) reported the Mississippi River had an average total Hg (THg) concentration of 19.94 pM in the lower river. Other studies report THg concentrations in sediment near the mouth of the Mississippi River ranging from 0.284 – 0.399 pmol/g (Neff, 2002). Krabbenhoft et al. (1999) reported average MMHg concentrations in water for areas in the Mississippi River Basin ranging from 0.0997 pM in Mobile River, AL and Trinity River, TX to 2.29 pM in the Acadian-Pontchartrain River Basin. Sediment MMHg concentrations in these same areas ranged from 0.249 – 3.24 pmol/g (Krabbenhoft et al., 1999). Neff (2002) concludes that MMHg in water and sediment of the Mississippi River Basin account for 21% and 0.2% of the total Hg, respectively. Using this figure, Neff (2002) calculates the Mississippi River discharges roughly 1496 mol/yr of MMHg to the Gulf of Mexico.

The drilling of oil wells in the Gulf of Mexico represents a source of THg that could be converted to MMHg under the right conditions. Barite muds used to drill these wells contain average Hg concentrations around 2.5 nmol/g, this Hg is primarily in the form of HgS and is bound to insoluble barite (Neff, 2002; Trefry et al., 2002). Trefry et al. (2002) found that although THg concentrations in sediment were considerably higher close to drilling sites, MMHg concentrations at most sites studied were similar to concentrations elsewhere in the Gulf. Neff (2002) concluded that drilling oil wells releases about 764 mol/yr of THg to the Gulf of Mexico, but he contends that a minimal amount, if any, of this is converted to MMHg. After examining sediment around six platforms and comparing MMHg concentrations to areas not affected by drilling muds,

Trefry et al. (2002) came to a similar conclusion. Trefry et al. (2002) did find elevated levels of MMHg at one of the six sites studied (1.42 ± 0.81 ng/g). This study is the only study to date examining MMHg concentrations around platforms, and since they did find elevated MMHg concentrations around one of the rigs, the possibility of barite muds as a source of MMHg cannot be completely ruled out.

Of the three possible MMHg sources in the Gulf of Mexico, the significance of the hypoxic zone remains the only unknown; in many ways, the area seems ideal for MMHg formation. Rowe et al. (2002) found a healthy community of SRB in the surficial sediments (0-8 cm) of the northern Gulf of Mexico; the presence of these microbes indicates that the hypoxic zone has the capability to methylate Hg. Since the area of the hypoxic zone is larger than the areas affected by direct Hg input from the Mississippi River or from areas surrounding oil rigs it seems that even minimal MMHg formation in this area would greatly impact the Gulf.

Research Objectives and Hypothesis

The main focus of this research was to demonstrate that the hypoxic zone is a region of enhanced MMHg production. Increased summer temperatures, strong freshwater fluxes, reduced dissolved oxygen concentrations, and increased suspended particle loads from the rivers combine to make the northeastern Gulf of Mexico ideal for MMHg formation. Given correlations established in other studies between the above mentioned environmental parameters and Hg methylation, it seems likely that spring and summer on the northeastern Texas-Louisiana shelf would be a time of enhanced MMHg production.

To address this question, a survey of the northeastern Texas-Louisiana shelf was conducted before, during, and after hypoxia formation to look for evidence of increased MMHg concentrations in the bottom water. Environmental conditions in the Gulf were evaluated against MMHg concentrations to establish possible links. Particular attention was given to the relationship between dissolved oxygen and MMHg concentrations because it is the environmental parameter that defines the hypoxic zone. This project also investigated the significance of MMHg fluxes from sediment into bottom waters relative to MMHg fluxes to the hypoxic zone from the Mississippi River and from precipitation.

METHODS

Sample Collection

Water samples and sediment cores were taken on a series of cruises aboard the *R/V Gyre* and *R/V Pelican* from April 2004 to May 2005. These cruises visited the hypoxic area off the Texas-Louisiana shelf during its formation, peak, and disappearance. Water samples and sediment cores were taken from each site. An attempt was made to revisit previously sampled sites when possible, but each month sampled contained a different number and combination of sampling sites (Table 1; Fig. 2). Between 3 and 13 sites were sampled each cruise. To eliminate some of the variability produced by inconsistent sampling, sites were grouped into geographic groups A, B, and C (Fig. 2).

Surface and bottom water samples were collected using Niskin bottles mounted vertically on a Rosette sampler. Bottom water samples collected on the *R/V Gyre* were collected when the bottle was centered 0.66 m above the sediment. Field blanks were collected, using deionized (DI) water, 3 – 4 times each cruise. Monomethylmercury blanks from uncleaned Niskin bottles were compared to blanks from an acid cleaned GoFlo bottle; blanks between the two bottles were comparable and sufficiently low. At each station filtered and unfiltered water samples were taken. A one liter aliquot of water was collected directly from the Niskin bottles and left unfiltered. A second liter sample was pumped from the Niskin bottle, through ultra clean Teflon tubing with a peristaltic pump, and filtered through an acid cleaned 0.45 µm polysulfone cartridge filter into an ultra clean Teflon bottle (Gill and Bruland, 1990). All samples were acidified with 0.2% low Hg HCl. All bottles were double bagged, stored in the dark, and kept cool until analysis (EPA Method 1669).

A box core was taken at each sampling site, and sediment sub-cores were collected from the box core using micro-washed core tubes. To gain a sense of the variability of MMHg in sediment, duplicate cores were taken throughout the sampling period. The top 10 cm of the cores were extruded, sectioned into 1 cm segments, stored in Whirl-Pak bags, and frozen until analysis.

Hydrographic Data

Dissolved oxygen, salinity, temperature, light intensity, and particle concentration in the water column were determined as part of the hydrographic data collected during the cruises.

The depth and intensity of the pycnocline were obtained by using CTD profiles taken at collection sites. The stratification intensity - measured by the Brunt-Vaisala frequency (N^2) - was calculated:

$$N^2\ (1/s^2) = \left(\frac{g}{\rho_o}\right)\left(\frac{\partial \rho}{\partial z}\right)$$

Where g is acceleration due to gravity, ρ_o is reference density taken as the average density of the entire water column, and $\frac{\partial \rho}{\partial z}$ is the change in potential density with depth.

Table 1. Sampling sites, their approximate location, and date sampled. W denotes sites where just water samples were taken. Sites 02A, 07A, 10A, 11A, 12A, and 16A are in Group A. Sites 07B, 10B, 12B, 17B, 18B, C4, C5, C6, C8, and C9 are in Group B. Sites 02C, 07C, 08C, 10C, and 16C are included in Group C. Samples collected in October 2004 were collected aboard the *R/V Pelican*, all other samples were collected aboard the *R/V Gyre*.

Site	Latitude	Longitude	April 2004	June-July 2004	August 2004	October 2004	March 2005	May 2005
02A	29.14	89.77			X		W	W
07A	29.12	89.54		X	X		X	X
10A	28.88	89.71		X	X			
11A	29.04	89.49						X
12A	28.96	89.51	X	X	X		X	X
16A	28.84	89.51		X	X			
07B	28.96	90.55			X			
10B	28.62	90.55			X		X	X
12B	28.86	90.41	X	X	X		X	X
17B	28.88	90.32					X	
18B	28.78	90.32			X			
02C	29.06	92.37					X	X
07C	29.12	91.91			X			
08C	29	92	X		X		X	X
10C	28.8	92.13			X			
16C	28.88	91.73		X	X		X	X
C4	28.57	90.31				W		
C5	28.54	90.29				W		
C6(B,C)	28.52	90.28, 90.29				X		
C8	28.47	90.16				W		
C9	28.45	90.14				W		

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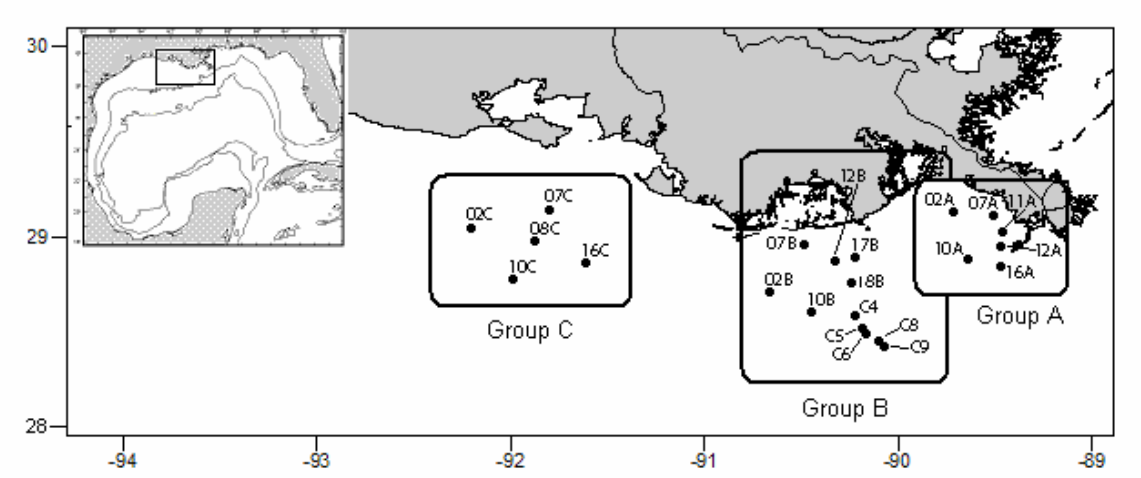

Fig. 2. Map of sampling sites along the Texas-Louisiana Shelf in the Gulf of Mexico. Sampling sites were split into three geographic groups to increase the power of statistical analyses. Group A is closest to the mouth of the Mississippi River. Group C was closest to the Atchafalya River, and Group B was between Groups A and C.

Monomethylmercury Analysis

Water samples were distilled using a 1% Ammonium Pyrrolidine DithioCarbamate (APDC) solution to isolate MMHg from the sample matrix (Liang et al., 1994; Bloom et al., 1997). Samples were distilled at 135°C and the distillate was collected in iced receiving vessels (Horvat et al., 1993a; Choe et al., 2004). Distillation rate was maintained at approximately 9 mL/hour until a total of 150 mL of distillate was recovered. Following distillation, the pH of the distillate was increased to 4.9 with acetate buffer, and a sodium tetraethyl borate, $NaB(C_2H_5)_4$, solution was added as an ethylating reagent (Horvat et al., 1993a). After a 20 minute reaction time, samples were purged with $Ar_{(g)}$ for 17 minutes at a flow rate averaging 300 mL/min, allowing the ethylated species to absorb onto a Tenax TA trap. Once dried, the column was connected to the inlet of a gas chromatograph. With an Ar carrier gas passing through the trap, it was heated, releasing the Hg species to the gas chromatograph. Separation of the mercury species was conducted isothermally on a 15% OV-3 Chromosorb W packing. The Hg species evolving from the gas chromatograph were destroyed at high temperature and detected using cold vapor atomic fluorescence spectroscopy (CVAFS) (Liang et al., 1994). Sample concentrations were calculated from peak areas obtained from a chromatographic software program (E-lab). This was done using response factors calculated from a 5-point calibration curve analyzed daily. Method blank concentrations and the percent of MMHg recovered in the samples (calculated using spiked samples) were also taken into account when calculating sample concentrations. Total MMHg is defined as the amount of MMHg detected in unfiltered water samples. Particulate MMHg is the difference in MMHg concentrations detected in filtered and unfiltered water samples.

MMHg extraction from sediment follows the procedure explained by Bloom et al. (1997). Approximately 0.5 g of sediment sample was mixed with 1 M $CuSO_4$ solution, digested with an acidified KBr solution, and extracted into 10 mL of CH_2Cl_2. After shaking and centrifugation, an aliquot of CH_2Cl_2 was added to 45 mL water for back extraction by purging with N_2 (g) for 35 minutes. The diluted sample was used for MMHg analysis by aqueous phase ethylation, collection onto Tenax columns, isothermal GC, and detection by CVAFS (Horvat et al, 1993b; Liang et al, 1994). The latter part of this procedure is similar to the aqueous MMHg analysis described previously. Monomethylmercury concentrations were calculated based on the CH_2Cl_2 dilution factor, sample recovery (calculated using spiked samples), and sediment water content. To determine the water content of the sediment, an aliquot was weighed and placed in a drying oven for 24 hours.

Total Mercury Analysis

Total Hg concentrations in sediment were measured using a Milestone direct mercury analyzer (DMA-80). An 11 point calibration curve was made using two standard reference materials (SRMs): MESS-2 (dried marine sediment, 92 ng Hg/g; National Research Council, Canada) and PACS-2 (dried marine sediment, 3040 ng Hg/g; National Research Council, Canada). Approximately 0.1 g of wet sediment was used for analysis (EPA Method 7473). Final concentrations were reported on a dry weight basis based on the water content of the sediment.

Benthic Flux Calculations

Benthic fluxes were estimated based on the change in bottom water total MMHg concentrations between sampling events $\left(\frac{\Delta MMHg}{\Delta t}\right)$. Flux was estimated by determining the change in Hg for a $1m^2$ section of the water column beneath the pycnocline. Several assumptions were made while estimating the benthic flux, the most important being that there was no horizontal water movement. It was also assumed that concentrations taken roughly 1 m from the sediment surface were representative of MMHg concentrations in the water column below the pycnocline, and that a negligible amount of water column methylation took place.

RESULTS

Data Validation

There currently exists no aqueous SRM for MMHg. For this project, the SRM DORM-2 (dried dogfish tissue, 4.64 µg MMHg/g; National Research Council, Canada) was digested with KOH and methanol and used as an aqueous MMHg SRM. Aqueous DORM-2 was analyzed daily with an average recovery of 98.0 ± 10.7% (n=61). DORM-2 was also used as a SRM for sediment MMHg with an average recovery of 95.7 ± 19.2% (n=20). MESS-1 (dried marine sediment, 91 ng Hg/g; National Research Council, Canada) and PACS-2 were used as SRMs for THg analysis of sediments with an average recovery of 100 ± 9.70% (n= 30).

Matrix spike recoveries were conducted for roughly 15% of all aqueous MMHg samples. The average matrix spike recovery for surface water was 91.1 ± 10.4% (n=38). For unknown reasons, the average recovery for bottom water was lower – 73.4 ± 22.6% (n=49). Matrix spike recoveries were conducted for roughly 10% of all sediment samples; the average MMHg matrix spike recovery for sediment was 98.5 ± 19.1% (n=38).

Detection limits were calculated as three times the standard deviation of method blanks run during analysis; for MMHg in water, the detection limit was 0.00416 pM (n=77), and for MMHg in sediment the detection limit was 0.0574 pmol/g (n=22). Method blanks were run each day of analysis.

All MMHg and THg concentrations reported for water and sediment at each site are averages of two or more individual analyses. Individual concentrations for a specific sample used to calculate the reported value contained no more than 10% difference.

Although the same general locations were sampled during each trip, it was impossible to sample the exact same sediment or water from month to month. To determine variability associated with sediment cores, 7 duplicate cores were taken throughout the sampling period. Duplicate cores were taken from the same box core, so they only represent variability existing within 0.25 m^2. The average relative percent difference (RPD) between duplicate core profiles (0-5 or 0-10 cm) was 39.1 ± 14.3%, and for duplicate surface samples (0-2 cm) the RPD was 35.2 ± 22.4%. Total Hg concentrations in surface sediment duplicates had an RPD of 37.0 ± 25.0 %. Most duplicate cores followed the same down core trends (Fig. 3). Unfortunately, duplicate water samples could not be collected; water samples collected are assumed to be representative of the immediate area.

Due to sampling limitations, water samples were not collected from ultra-clean, Teflon-coated Niskin bottles. Instead, they were collected from well flushed uncleaned Niskin bottles. To monitor the cleanliness of bottles used, field blanks – from ultra-clean and uncleaned bottles - were taken periodically. After rinsing bottles with DI water, low-Hg DI water was poured into the sampling bottles and collected as a field blank sample. Field blanks taken from both ultra-clean and flushed Niskin bottles showed similarly low levels of MMHg contamination (clean: 0.0150 pM, flushed: 0.00997 pM). After it was established that flushed Niskin bottles were as uncontaminated as ultra-clean sampling bottles, field blanks were only taken from flushed Niskins. The average field blank for the sampling period was 0.00997 pM (n=15), which was taken into account when reporting aqueous MMHg values.

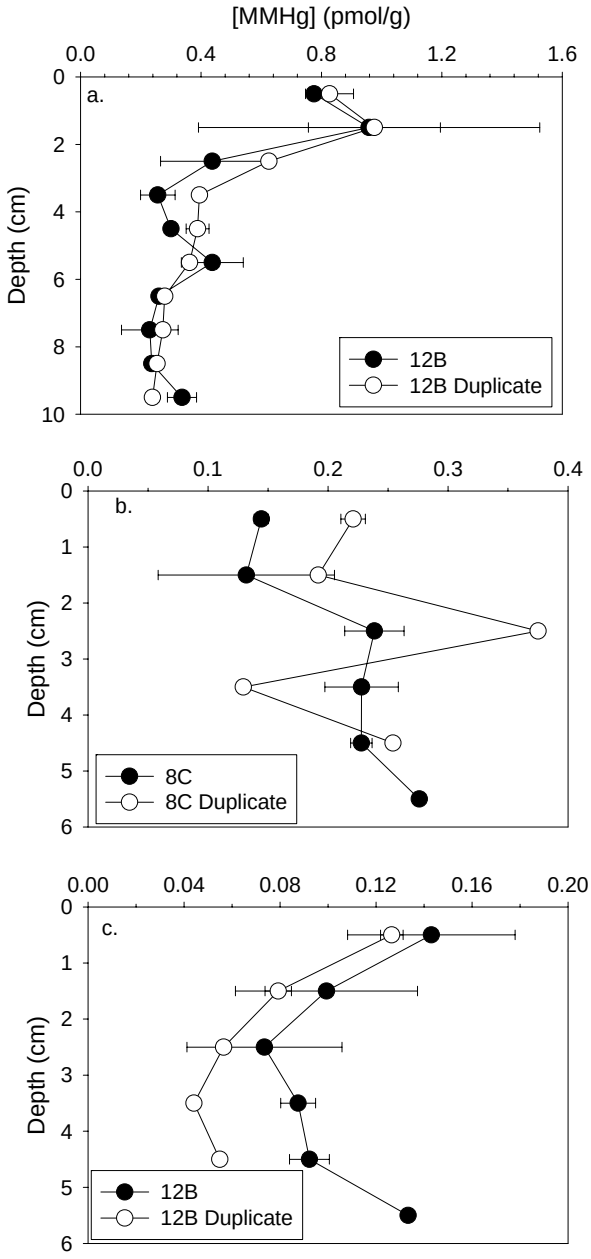

Fig. 3. a. Duplicate cores taken in June 2004 at site 12B. The RPD for the surface 2 cm was 4.15% and was 19.6% for the entire core. b. Duplicate cores taken in May 2005 at site 8C. The RPD for surface sediment was 39.5%, while the RPD for the entire core was 37.9%. c. Duplicate cores taken in May 2005 at site 12B. The RPD for surface sediments was 17.3%, and for the entire core the RPD was 35.5%. Error bars in all graphs represent one standard deviation calculated from multiple analyses at that particular depth. Error bars were not included at some depths because only duplicate analyses were done for that sample.

Temporal Variability

Surface Water

Total MMHg concentrations ([TMMHg]) varied little in surface water over time with a range of 0.0419 pM (Fig. 4). Particulate MMHg concentrations ([PMMHg]) in surface waters were highest in August 2004. Concentrations decreased in October 2004, and increased slightly in March and May 2005 (Fig. 5). Particulate MMHg was not collected during April or June/July 2004 sampling trips. Changes in PMMHg were small in scale, with a range of only 0.0563 pM.

Bottom Water

Bottom water data contained two outliers that biased averages of April and June/July 2004 TMMHg concentrations. In April, at site 12A, MMHg concentrations were 0.150 pM, and in June/July concentrations were 0.329 pM at site 07A. These data points were included in all statistical analyses and graphs; all trends still hold true – although weaker - when they are excluded.

Statistical analyses indicated that surface and bottom water total and particulate MMHg concentrations at each site were significantly different (Paired Comparisons t-Test, TMMHg: $t = -2.52$, $df=42$, $p<.05$, PMMHg: $t=2.87$, $df=35$, $p<.01$). Temporal differences in bottom water total MMHg concentrations were greater than changes in surface water concentrations, although they still represent a relatively small range: 0.319 pM (Fig. 4). Changes in bottom water total MMHg concentrations indicate a trend, although the trend falls short of being statistically significant (Pearson's Product-Moment Correlation Analysis: $r=-0.076$, $p=0.620$, $n=45$). Total MMHg concentrations peaked during June/July 2004 and decreased to a minimum in October 2004. Concentrations began to increase during the spring and early summer of 2005.

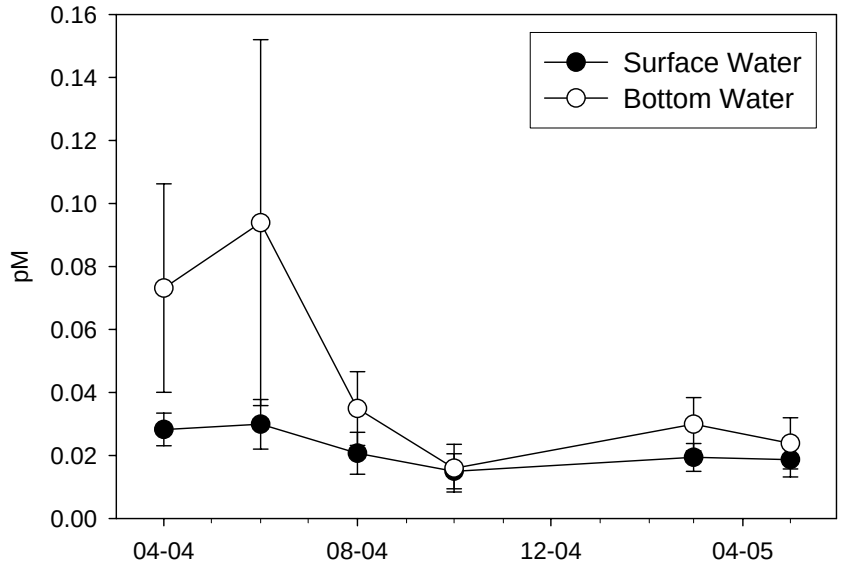

Fig 4. Average TMMHg concentrations in the surface and bottom waters as a function of time. Error bars represent one standard deviation of sites sampled each month: 3 sites in April 2004, 6 sites in June/July 2004, 13 sites in August 2004, 5 sites in October 2004, and 9 sites in both March and May 2005.

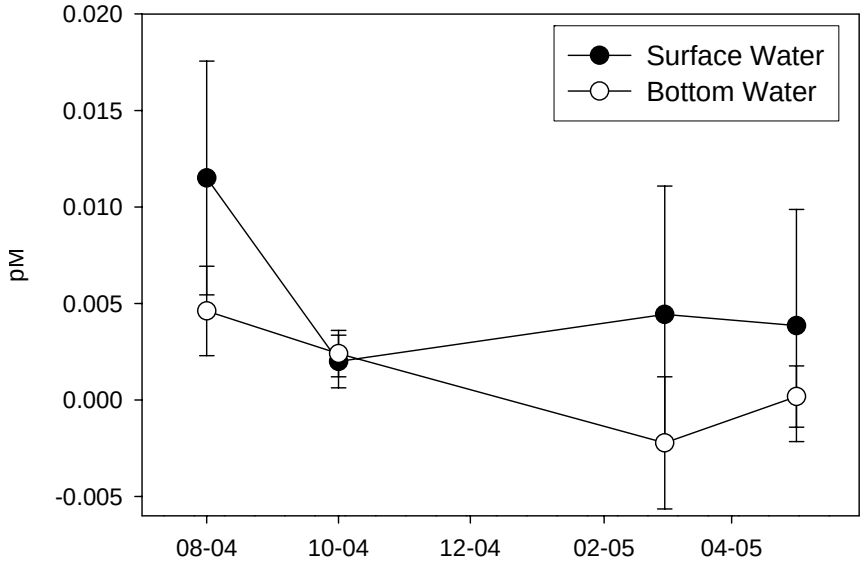

Fig. 5. Average PMMHg concentrations in surface and bottom waters as a function of time. Error bars represent one standard deviation of sites collected that month: 13 sites in August 2004, 5 sites in October 2004, and 9 sites in March and May 2005.

Bottom water particulate MMHg concentrations are correlated with time (Spearman's Rank Order Correlation; r_s= 0.511, p<.01, n=34), although concentration differences are on a femtomolar scale (Fig. 5). Temporal trends in particulate MMHg concentrations are similar to those described for total MMHg concentrations.

Sediment

During warmer months of June/July 2004, August 2004, and May 2005, elevated MMHg concentrations can be seen in the top 1 or 2 cm of most sediment profiles (Fig. 6). Although total Hg concentrations in surface sediment (0-2 cm) displayed more variability then total Hg in deeper sediment (10 cm), there were not any clear changes in total Hg concentrations with season (Fig. 7).

Background concentrations of MMHg (taken at 10 cm) in sediment stayed fairly constant with time and space: 0.975 ± 0.502 pmol/g. Total Hg background concentrations also stayed constant with time, averaging 178 ± 98.3 pmol/g. Small seasonal shifts can be noticed in the upper 5 cm of most profiles but the surface 2 cm changed most dramatically with time.

As can be seen in Fig. 8, monthly averages of MMHg concentrations in surface sediment (0-2 cm) and bottom water follow a similar trend throughout the sampling period. Spearman's Rank Order Correlation Analysis confirms the two measurements are similar (r_s=0.409, p<.05, n=36). Averages of surface sediment (0-2 cm) MMHg concentrations were most elevated in June/July 2004, and then decreased through the late summer and into winter. In spring and early summer 2005, sediment concentrations increased slightly.

The highest concentration of MMHg as a percent of THg in surface sediment occurred from April to August 2004; for these months an average of 7.5% of the THg was in the form of MMHg. This percentage drops to 2.7% during October 2004, and begins to increase during March and May 2005. In May, MMHg accounted for 5.3% of the THg (Fig. 9).

Benthic Flux

Seven sites were sampled frequently enough to make benthic flux calculations: 02A, 07A, 12A, 10B, 12B, 08C, and 16C (Table 2). Trends at each site and within each group are unique. Overall flux calculations show a negative flux in the spring, a slight increase during summer, and a positive net flux from August 2004 to March 2005. Fluxes vary with location in early summer 2005.

Spatial Variability

Surface Water

Statistical tests determined surface water total MMHg concentrations were elevated in Group A, while concentrations in Groups B and C contained similar concentrations (ANCOVA, $F= 3.40$, $p<.05$, $df= 2$). Surface TMMHg concentrations in Group A were highest during the April and June/July 2004 collection trips, 0.040 and 0.032 pM respectively. TMMHg concentrations in Groups B and C averaged to 0.021 pM during these months. Particulate MMHg concentrations in surface water did not vary with group.

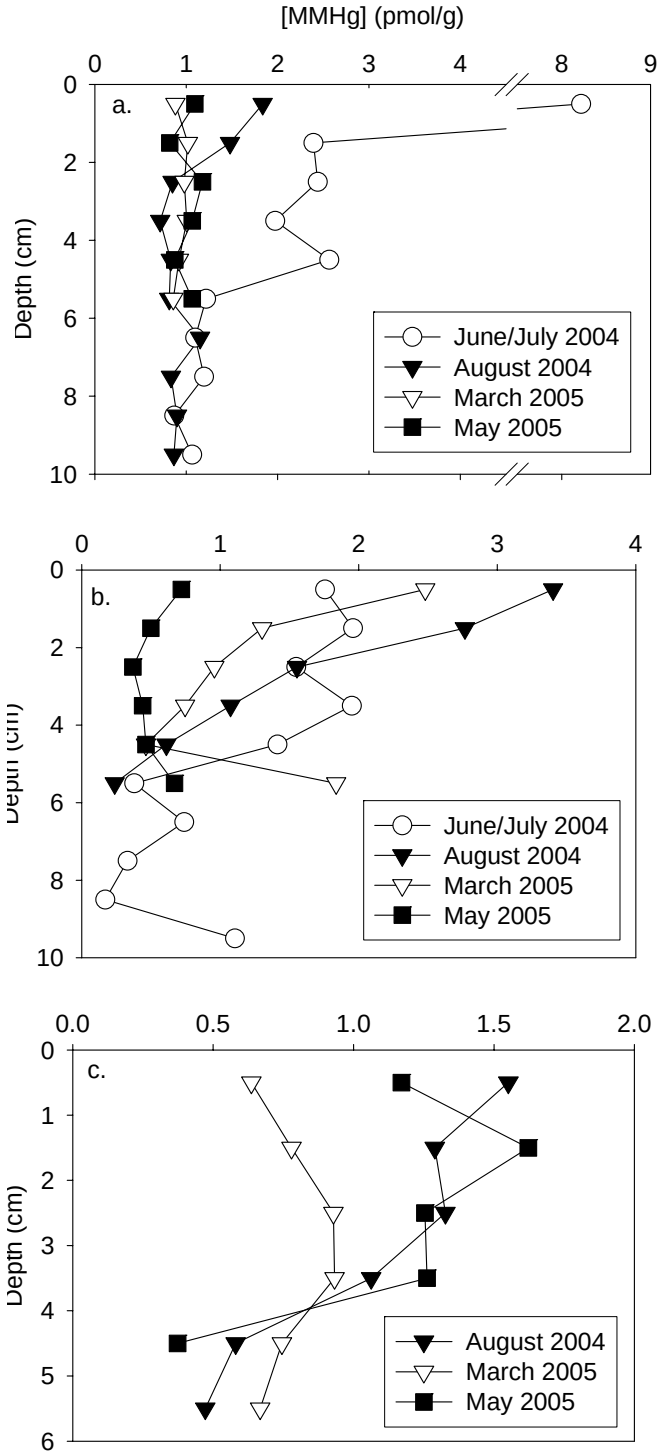

Fig. 6. Sediment MMHg concentration profiles for sites 12A (a.), 12B (b.), and 16C (c.). Error bars were omitted from these graphs for clarity.

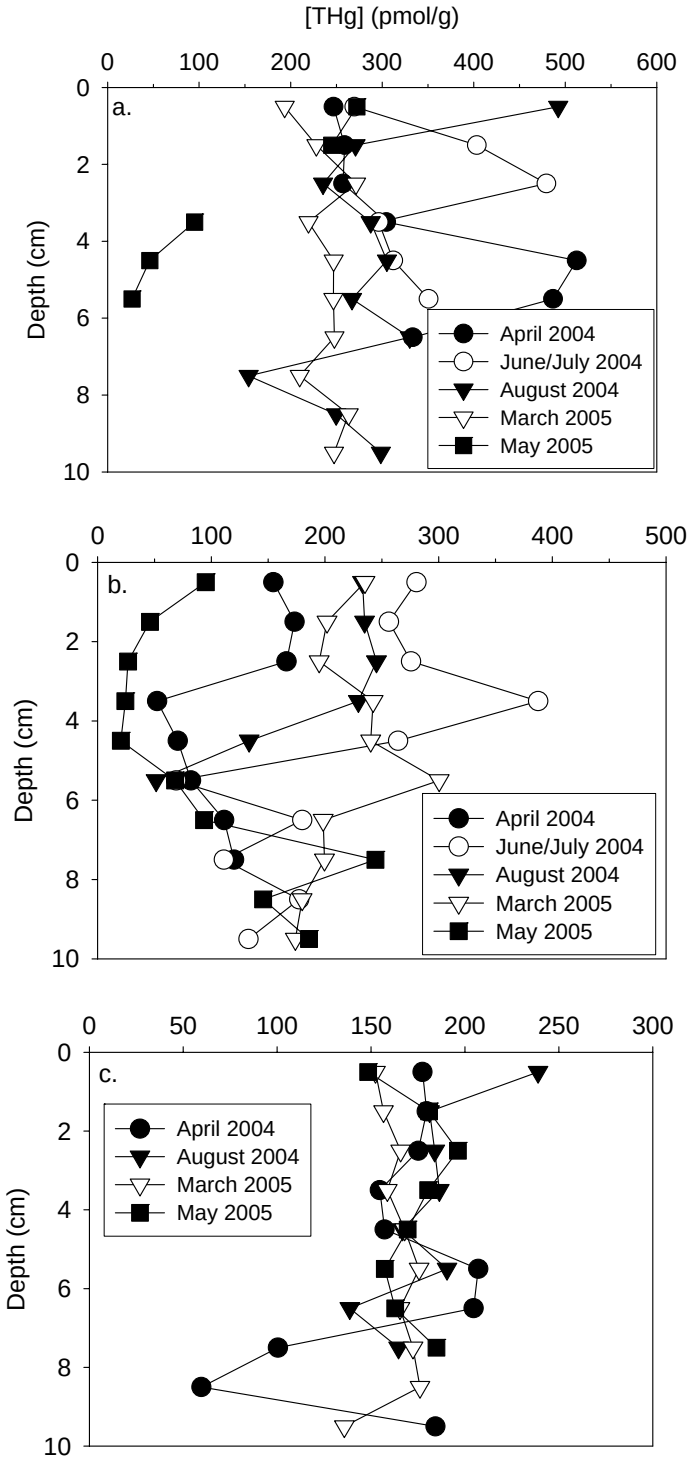

Fig 7. Sediment THg profiles for sites 12A (a.), 12B (b.), and 8C (c.). Error bars were omitted from these graphs for clarity.

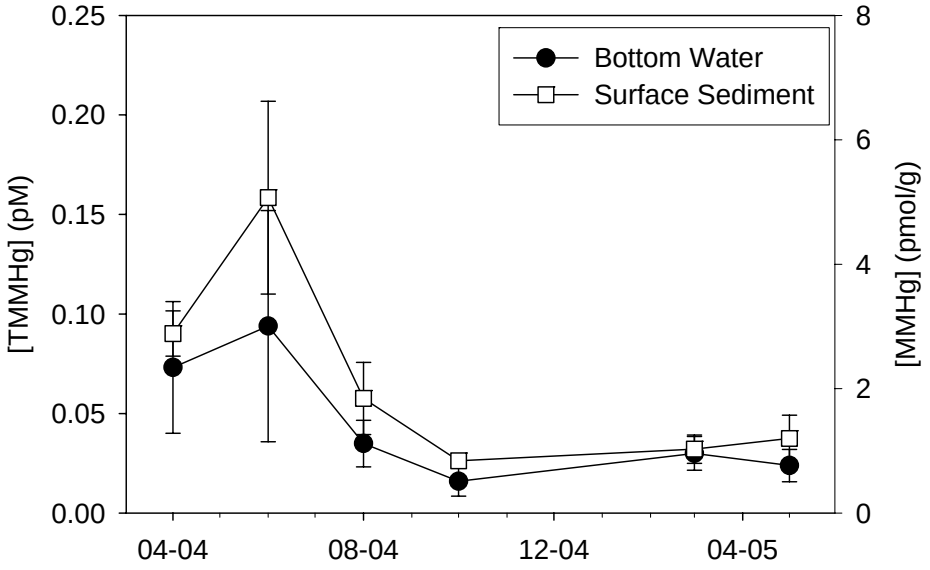

Fig. 8. MMHg concentrations in bottom water and surface sediment (0-2 cm) as a function of time. Error bars represent one standard deviation for all sites collected that month. In April, June/July, and August 2004 the number of water and sediment samples taken were equivalent. In October 2004, water samples were collected at 5 sites while only one sediment core was collected. In March and May 2005 9 individual water samples were collected and 8 sediment samples were collected.

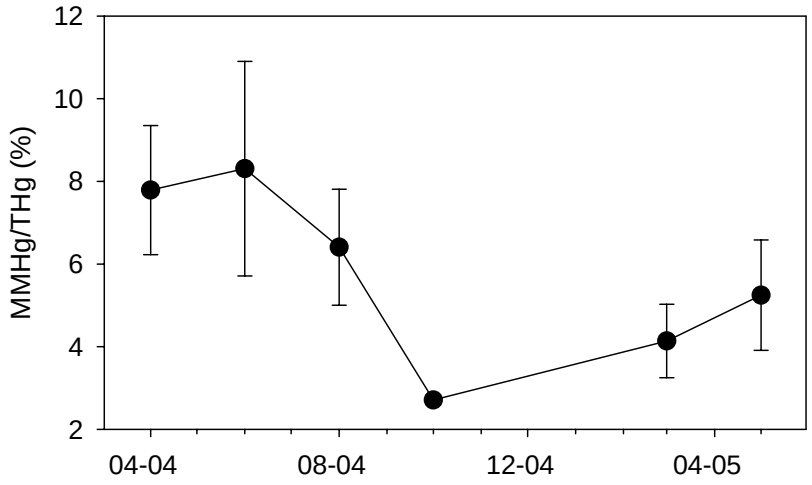

Fig. 9. Percent of THg present as MMHg in surface sediment over time. Error bars represent one standard deviation for all sites collected that month.

Bottom Water

Average total MMHg concentrations in the bottom waters of Groups A, B, and C were not significantly different (ANCOVA: F= 2.52, p=0.093, df= 2), but location did account for roughly 10.9% of the TMMHg variability. Averages are given in Table 3 and are graphed by group in Fig. 10. Although not statistically different, bottom water TMMHg concentrations were elevated during the first two sampling periods in Group A (Fig. 10). As mentioned previously, these averages are somewhat skewed because of two data points reflecting elevated MMHg concentrations. When these points are excluded, April 2004 total MMHg concentrations in Group A are decreased by 0.0382 pM and the June/July 2004 average is decreased by 0.047 pM. Concentrations of particulate MMHg in the bottom water are not significantly different between groups.

Sediment

MMHg concentrations in the surface sediment of Group A were significantly different from the concentrations in other groups (ANCOVA: F=3.82, p<.05, df= 2). Average concentrations in the surface sediment of Group A were 0.161 pmol/g higher than Group B sediments and 0.190 pmol/g higher than in Group C. Trends in surface sediments again echo those seen in the bottom water (Fig. 10).

Once divided into three sampling groups, localized trends in the surface sediment begin to appear. In Group A, MMHg concentrations increased dramatically in June/July 2004 reaching a concentration of 6.14 pmol/g (Fig. 11). MMHg concentrations decrease from June/July to August, reach a minimum in March 2005, and show a slight increase in May. The percent of THg in the form of MMHg in Group A increased from 4.2% to 9.9% between April and June/July 2004. The percent of MMHg decreased somewhat in August 2004 (5.7%). There is no data covering fall and winter months for Group A, but MMHg:THg ratios were lowest in the spring of 2005 (2.2%), and began to increase by May 2005 (4.8%).

Table 2. Benthic fluxes for seven sites in the Gulf of Mexico. Fluxes are given in pmol MMHg m^{-2} day^{-1}, dashes indicate no data.

Site	April - June 2004	June - August 2004	August 2004- March 2005	March - May 2005
02A	--	--	-0.185	-2.57
07A	--	-16.0	0.058	0.288
12A	-12.8	-2.49	0.000	-4.06
10B	--	--	0.967	-4.15
12B	-1.54	9.81	0.976	-5.89
08C	-2.34 (April - August 2004)		0.000	3.81
16C	--	-5.70	0.815	-1.77

Table 3. Average monthly concentrations (pM) of bottom water TMMHg by group and for all sites 'Combined'.

	Group A	Group B	Group C	Combined
April 2004	0.150	0.035	0.035	0.073
June/July 2004	0.148	0.025	0.040	0.094
August 2004	0.037	0.032	0.035	0.035
October 2004	--	0.016	--	0.016
March 2005	0.035	0.023	0.022	0.030
May 2005	0.027	0.023	0.021	0.024

Trends in MMHg concentrations in Group B stayed more constant with time; they did not show a summer increase and had a range of only 2.68 pmol/g (Fig. 11). In April 2004, the MMHg averaged 9.1% of the THg, decreased in June/July to 3.5%, and then increased again in August 2004 to 8.0%. The ratio decreased to a minimum in October (2.7%) and steadily increased through March and May 2005.

There is less data available for Group C (no cores were taken in this group in June/July or October 2004), but available data suggests trends similar to those found in Group A (Fig. 11). MMHg concentrations were highest in April 2004 (3.58 pmol/g), then they decreased significantly in August 2004 and stayed low throughout the rest of the sampling period. In April and August 2004, MMHg comprised an average of 7.8% of the THg. In March 2005 this dropped to 4.6%, and did not increase by May.

Influence of Environmental Parameters

Water temperature, salinity, dissolved oxygen (DO), photosynthetically active radiation (PAR), and particle concentrations were measured throughout the sampling period (Fig. 12). As might be expected, differences in surface water measurements for all parameters were more noticeable from month to month than bottom water variations. The most dramatic changes in bottom water characteristics were in temperature (a range of 6.61 °C) and DO (a range of 2.47 mL/L). Since these are the only parameters displaying any change with time, discussion of the influence of environmental parameters will largely focus on differences in temperature and DO.

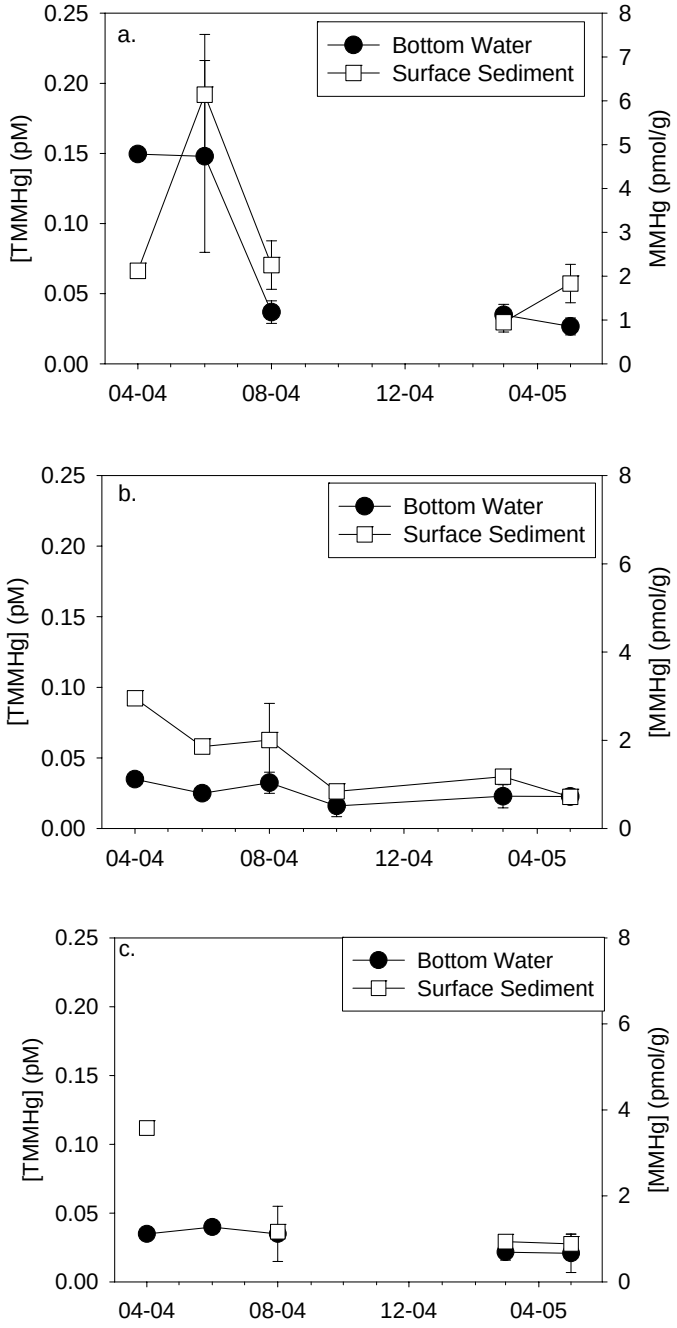

Fig. 10. Average MMHg concentrations in bottom water and surface sediment with time for each geographic group: Group A (a.), Group B (b.), and Group C (c.). Error bars represent one standard deviation of all sites analyzed in that group each month. Error bars were not included for those months where less than 3 sampling sites were available in a group.

Temperature

Although none of the above mentioned parameters are statistically correlated with bottom water total MMHg concentrations (Pearson's Product-Moment Correlation Analysis: MMHg,DO: r = -0.023, p=0.886, n=40; MMHg,temperature: r = 0.111, p=0.466, n=45), graphing temporal changes in temperature and DO along with bottom water total MMHg concentrations reveals a relationship (Fig. 13). Bottom water total MMHg concentrations and temperature seem to be inversely correlated: MMHg concentrations spiked in June/July 2004 as bottom water temperatures were warming. In October, bottom water TMMHg reached its lowest concentration while temperature reached a maximum. TMMHg concentrations increased slightly after October 2004 while water temperatures decreased until spring 2005. A scatterplot of this data displays a slight positive relationship, indicating that increases in temperature, overall, did increase MMHg concentration (Fig. 14a).

Dissolved Oxygen

Dissolved oxygen concentrations exhibited an inverse relationship with bottom water total MMHg concentrations (Fig. 13). While total MMHg concentrations were increasing in summer 2004, average DO concentrations decreased to a minimum: 1.36 mL/L, which is hypoxic. After a mid-summer spike, total MMHg concentrations decreased until October, DO increased during this time to 2.60 mL/L. Both DO and total MMHg concentrations stayed relatively constant through late spring 2005.

During this study samples were collected at 12 hypoxic and 33 oxic sites. These unbalanced numbers should be kept in mind when examining Figs. 15 and 16; hypoxic bottom water concentrations represent relatively few events (2-7 samples depending on group) while a majority of oxic readings are an average of twice as many samples. Even given this limited data, trends can be seen. Overall, hypoxic sites in Groups A and C had substantially elevated levels of TMMHg when compared to oxic sites (Fig. 15). TMMHg concentrations between oxic and hypoxic sites in Group B varied by only 0.004 pM. Fig. 14b shows evidence that supports this relationship, displaying a slightly negative relationship between bottom water DO and MMHg concentration.

Trends can also be seen in surface sediment at oxic and hypoxic sites. Group averages clearly show that MMHg concentrations were higher in oxic sediment (Fig. 16). Groups A and C also show THg concentrations are higher in oxic sediment, while Group B averages indicate that hypoxic sediments contained 42.1 pmol/g more THg than oxygenated sediments. MMHg is a slightly higher fraction of the THg in hypoxic sediment versus oxic sediment; again, Group B shows the opposite to be true.

Stratification

Total MMHg concentrations in bottom water is positively correlated with the intensity of the pycnocline (Pearson's Product-Moment Correlation Analysis; $r = 0.479$, $p < .01$, $n = 45$; Fig. 13). Scatterplots of stratification intensity and bottom water total MMHg concentrations also indicate there is a relationship between the two parameters (Fig. 14c). Both stratification intensity and total MMHg concentration increased to a maximum in June/July 2004. Minimum measurements for both parameters were recorded in August 2004, and both steadily increased for the remainder of the sampling period.

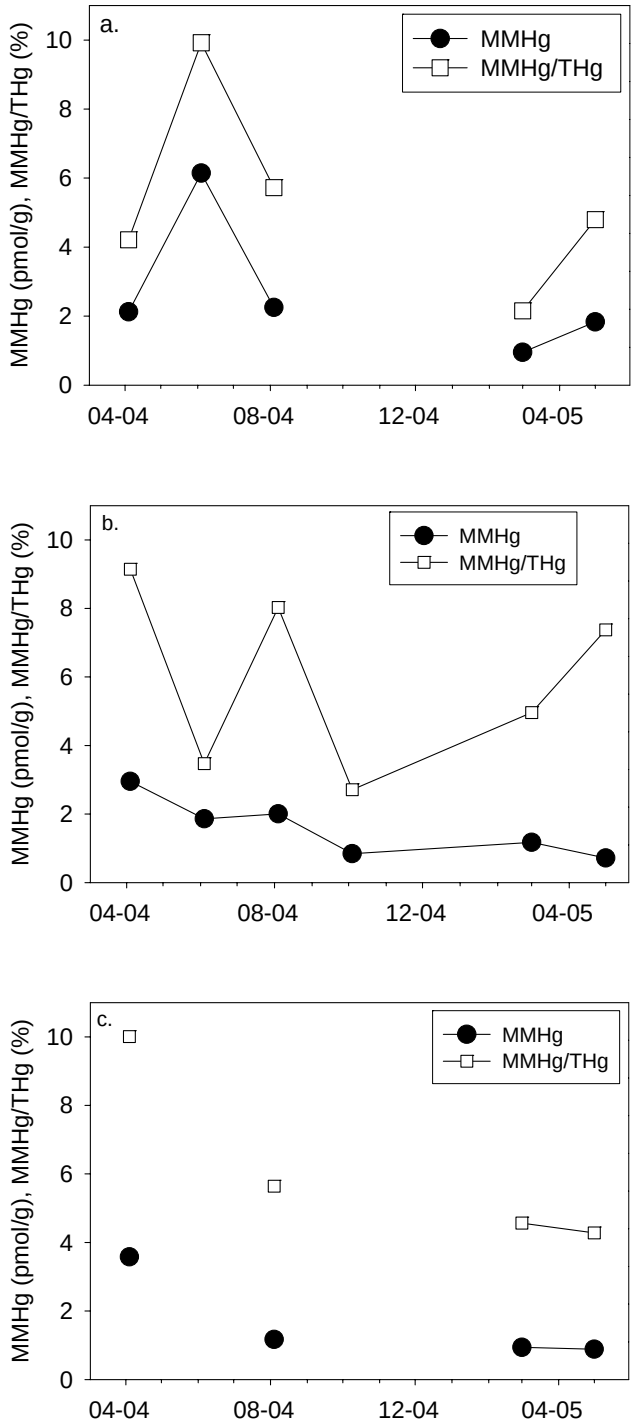

Fig. 11. Average MMHg concentrations and percent MMHg in surface sediment (0-2 cm) for Group A (a.), Group B (b.), and Group C (c.). Error bars were excluded from these graphs for clarity.

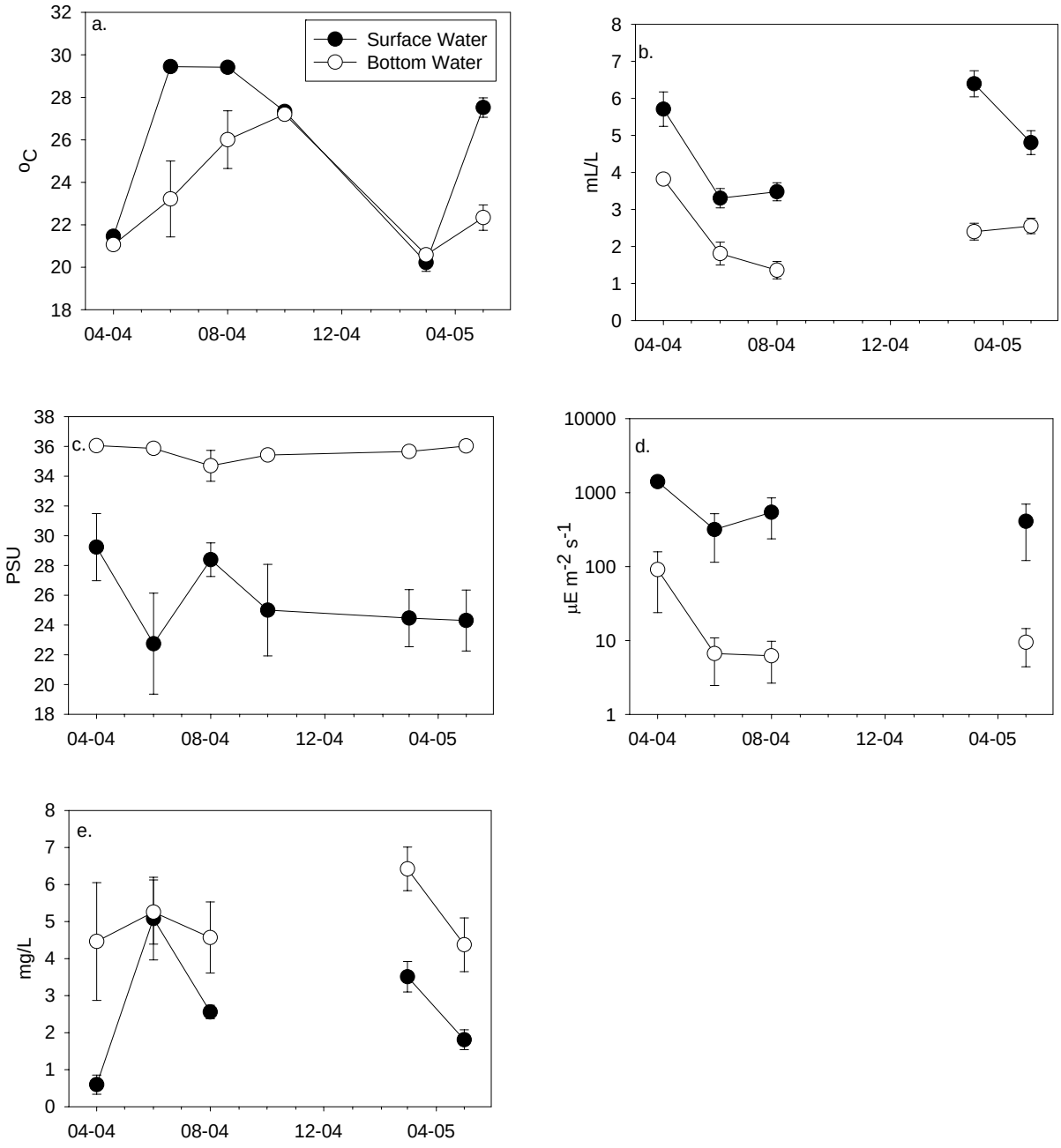

Fig. 12. Monthly averages of temperature (a.), dissolved oxygen (b.), salinity (c.), light intensity (d.), and particle concentration (e.) in surface and bottom water for all sampling sites from April 2004 to May 2005. Error bars represent one standard deviation for all sites sampled that month.

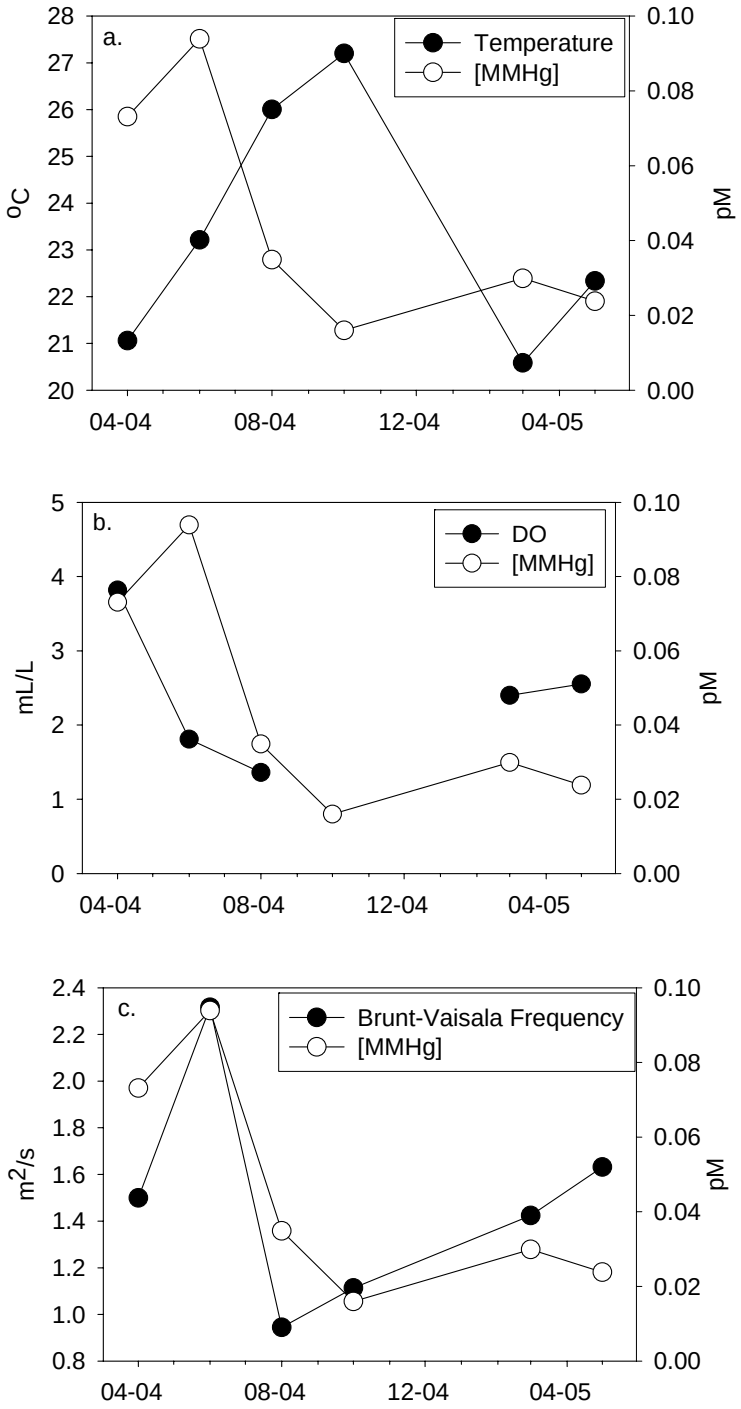

Fig.13. Monthly averages of bottom water temperature (a.), dissolved oxygen (b.), or stratification intensity (c.) compared with MMHg concentrations at all sites measured as a function of time. For clarity, error bars were excluded from these graphs.

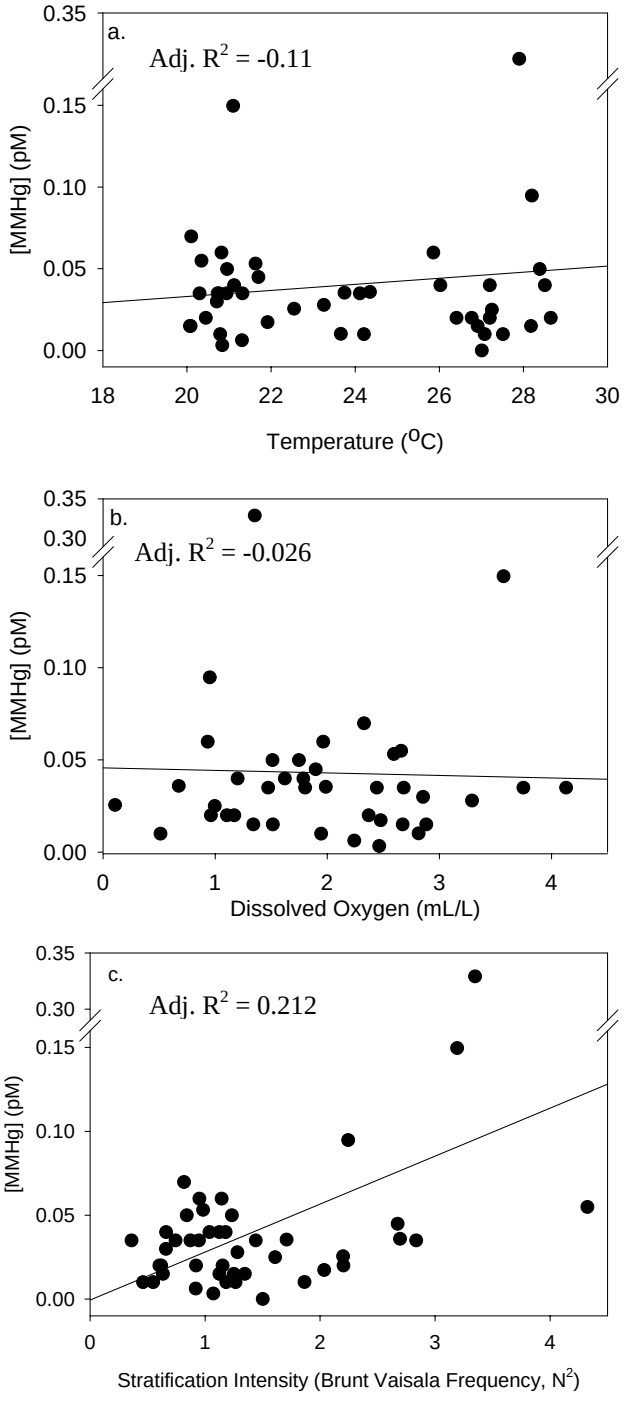

Fig.14. Plots depicting the relationship between key environmental parameters – bottom water temperature (a.), bottom water DO (b.), or stratification intensity (c.) - and bottom water MMHg concentrations. Graphs include data from every site visited during the course of this study and a best-fit line with R^2 value.

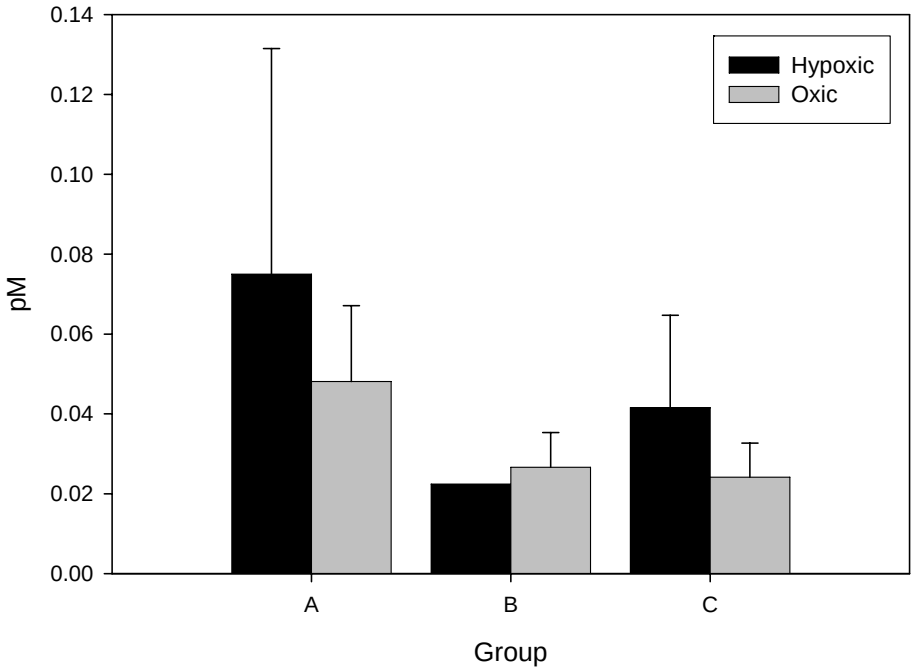

Fig.15. Group averages of bottom water total MMHg concentrations during oxic and hypoxic events. During one or more months sampled sites 02A, 07A, 11A, 16A, 10B, 12B 07C, 10C, and 16C were hypoxic; concentrations under hypoxic and oxic conditions were averaged for those sites, and are displayed independent of time.

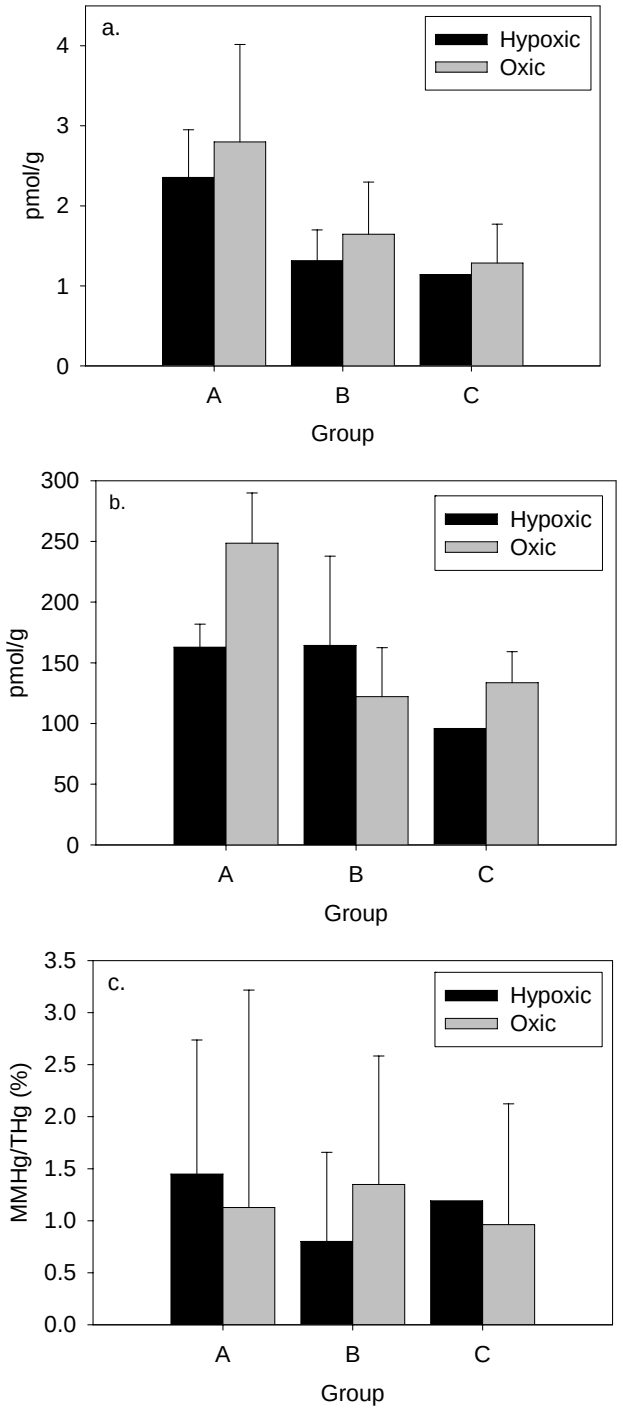

Fig. 16. Group averages of surface sediment MMHg concentrations (a.), total Hg concentrations (b.), and the percent MMHg contributing to THg (c.) at oxic and hypoxic sites. Any site sampled that contained a hypoxic event was included in these averages.

The depth of the pycnocline also changed with time. In April, the pycnocline, if present, was quite shallow; this was also the case in October 2004. During June/July 2004, March 2005, and May 2005 an average of 35% of the water column was below the pycnocline. In August, most sites were unstratified, approximately 42% of the water column was below the pycnocline at those sites that were stratified.

Salinity, PAR, and Suspended Particle Concentration

Salinity in bottom water varied little throughout the sampling period (average: 35.4 ± 1.26 PSU) so any relationship between bottom water salinity and total MMHg was undetectable. Plots of surface salinity vs total MMHg concentration (not shown) display a slight decrease in total MMHg concentration with increasing salinity (R^2=0.0279).

There was no difference in total MMHg concentrations in surface samples collected during the night or day (Group Comparison t-Test: t=0.0256, p=0.980, df=27). Again, PAR did not vary greatly in bottom waters, so no correlation could be detected.

Surface and bottom water total and particulate MMHg concentrations displayed a slight increase with increases in suspended particle concentration. This trend was more pronounced in surface waters (TMMHg: R^2=0.053; PMMHg: R^2=0.113), but was noticeable in bottom water as well (TMMHg: R^2=0.0175; PMMHg: R^2=0.0006).

DISCUSSION

Temporal Variability - Yearly Variations

Increased river flow into the Gulf of Mexico in the spring usually marks the beginning of summer hypoxia formation. The timing and amplitude of maximum river input determines, to some degree, the severity and spatial extent of the hypoxic zone, as well as the timing of its development (Rabalais et al., 2001). In a typical year, the Mississippi and Atchafalaya Rivers gradually increase their discharge rates to a maximum in April; flow generally decline through August and remain low until discharge increases in November (Fig. 17).

In 2004, the timing of river discharge was typical: increasing in November and decreasing in July. River flow rates never reached a peak, but remained high from February to late July 2004. The following year, maximum river flow was early, in late December 2004/early January 2005 (Fig. 17). This time difference is important in considering the formation of hypoxia and peak MMHg concentration between the two years.

Rabalais and Turner (2001) state that there is a two month time lag between river discharge and the onset of hypoxia; using this rough time scale, stratification and depletion of bottom water oxygen would have started in January 2004 and in Feburary or March 2005. In 2004, peak MMHg concentrations occurred in June/July 2004, 7 months after maximum river flow and roughly 5 months after the onset of hypoxia. Using 2004 MMHg trends as a timeline, peak MMHg concentrations would have been expected to occur in July or August 2005. River discharge and hypoxia formation was late in 2005 so bottom water MMHg concentration had not reached a peak when sampling stopped in May.

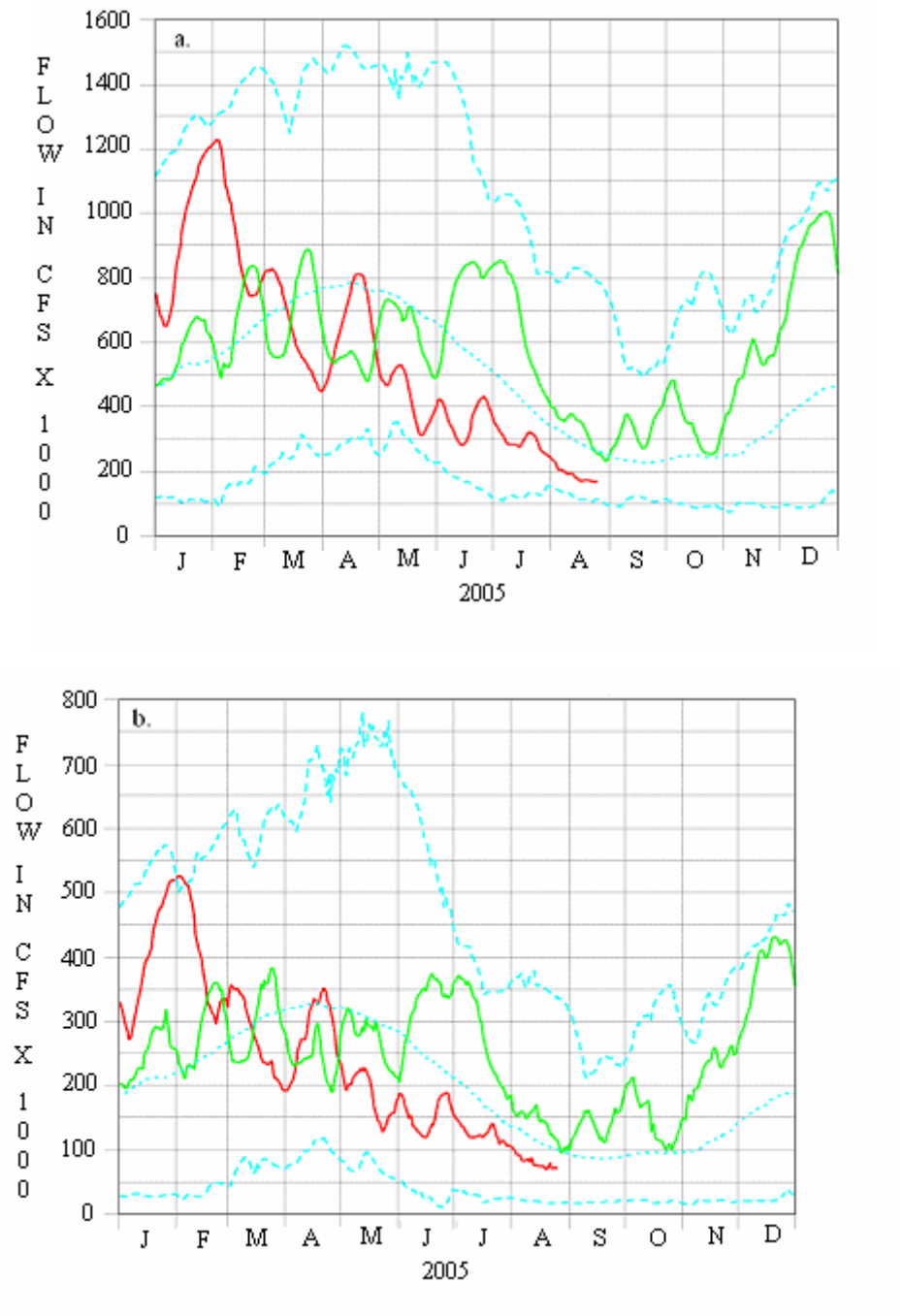

Fig. 17. Mississippi River discharge hydrographs taken at Tarbert Landing (a.) and Atchafayla River discharge hydrographs taken at Simmesport (b.) during 2004 and 2005. Green lines indicate 2004 flow and red lines represent 2005 flow. Blue dotted lines are average, maximum, and minimum river discharge. Graphs taken from US Army Corps of Engineers, New Orleans District.

River flow rates also varied between 2004 and 2005. In 2004, river flow was maintained around 19,800 m^3/s for 7 months, and in 2005 flow stayed at or above this rate for only 3.5 months; maximum flow was about 27,500 m^3/s. High river flow lasted two times longer in 2004 and could explain lower surface water salinity and higher stratification intensities in the spring and summer of that year; this would also explain differences in MMHg concentrations between the two years. Changes in the timing and volume of river flow may also help explain differences in sediment MMHg concentrations in 2004 and 2005.

It is logical that the timing, and possibly the extent, of Hg methylation depends on when the northern Gulf becomes stratified. There were dramatic differences in the biogeochemical parameters controlling the region in spring 2004 verses 2005 and it is assumed that these differences also influenced MMHg formation rates and seasonal concentrations. It is also worthwhile to note that the river flow trends for these two years are not typical (Fig. 17), which may also mean that MMHg concentrations in the Gulf during these times were also abnormal.

Temporal Variability - Seasonal Variations

In the Gulf of Mexico, stratification separates surface and bottom waters for a majority of the year (Rabalais et al., 2001). This separation, and the effect of differing environmental conditions in the two water stratum, causes surface and bottom waters to act essentially as separate water bodies controlled by distinctly separate physical and biogeochemical parameters.

Surface Water

MMHg concentrations in surface water of the northern Gulf of Mexico remained relatively constant throughout the year. This is typical for most stratified water systems (e.g. Jacobs et al., 1995; Eckley and Hintelmann, 2005) and was expected in the Gulf of Mexico. Surface water TMMHg concentrations were almost 5 times lower than bottom water concentrations during spring and summer months. Horvat et al. (1999) noticed this trend in the Gulf of Trieste, stating that surface water concentrations were 10 times lower than those in bottom waters. Again, this observation is typical for most unpolluted water bodies (Watras and Bloom, 1995; Faganeli et al., 2003; Eckley and Hintelmann, 2005) and was expected to occur in the Gulf.

Differences between surface and bottom water MMHg concentrations are commonly attributed to higher benthic methylation rates affecting bottom water concentrations (Wiener et al., 2003). In warmer months, when methylation has increased, stratification isolates surface water from the sediment – the most likely source of MMHg (Mason et al., 1999; Faganeli et al., 2003) – causing bottom water concentrations to increase while surface water concentrations stay constant. During fall and winter after stratification breaks down, there is much less MMHg being produced (Leermakers et al., 2001), keeping surface MMHg concentrations low. Given TMMHg concentration trends seen in the Gulf of Mexico, this is a likely explanation for the low variability of surface water TMMHg when compared to bottom water concentrations.

Photodemethylation takes place in surface waters and has been proposed as an important mechanism of MMHg removal from surface waters (Sellers et al., 1996). Microbial demethylation, although not unique to surface water, is another important mechanism of eliminating MMHg from surface waters (Matilainen and Verta, 1995).

Incorporation of MMHg into the food web (Mason et al., 1996) and adsorption onto sinking particles (Ullrich et al., 2001) are also effective means of MMHg removal from the water column. Although none of these parameters were directly measured, they could also help explain the low variability in surface water TMMHg concentrations.

Bottom Water

Many studies of seasonally stratified, anoxic water bodies have reported maximum bottom water MMHg concentrations during the summer months followed by a winter minimum (e.g. Jacobs et al., 1995; Hintelmann and Wilken, 1995; Leermakers et al., 2001). As was hypothesized, MMHg concentrations in the Gulf of Mexico seem to conform to these typical temporal trends; bottom water MMHg concentrations reached a maximum in June/July, decreased in October, and were beginning to increase again in May. In other studies, these seasonal changes have been most commonly attributed to:
1) increased methylation - in the water column as well as the sediment - due to decreased oxygen and increased temperature (Gilmour and Henry, 1991). As stated earlier, methylation is a microbially mediated, anaerobic process influenced by temperature and DO. Increases in temperature stimulate more bacterial activity, while decreases in DO provide a suitable environment for bacterial growth. 2) Deposition of MMHg with settling matter. MMHg is a particle reactive species, so in an area like the hypoxic zone that is affected by seasonal eutrophication and large changes in suspended particle load, this could be a significant source of MMHg variation. 3) Increased MMHg flux from sediment into overlying water often occurs under low oxygen conditions (Horvat et al., 1999), although it is also associated with changes in light levels (Gill et al., 1999), temperature fluctuations (Covelli et al., 1999), and pH (Boszke et al., 2003). All three of these processes are factors which might be contributing to seasonal MMHg trends seen in the Gulf of Mexico.

MMHg concentrations are the net result of methylation and demethylation. In the winter, demethylation is typically greater than methylation, resulting in minimal MMHg concentrations (Korthals and Winfry, 1987; Gilmour et al., 1998). Increases in demethylation are likely due to high oxygen saturation, increased salinity, cooler temperatures, and decreased OM. Also, during the winter, processes such as MMHg diffusion from the sediment may shut down or decrease, limiting TMMHg concentrations in bottom waters (Ullrich et al., 2001). Although demethylation was not measured in this study, the decrease in TMMHg during the late fall 2004 was likely effected by increases in demethylation rates.

Bottom water temperature and DO were expected to greatly influence these MMHg variations. Temperature and DO did seem to have some impact on MMHg concentration, but they did not control concentrations to as great an extent as was hypothesized. During the June/July 2004 sampling trip, average bottom water temperature was 23.89ºC and average DO was 1.81 mL/L. In August, the average temperature was warmer (26.0ºC) and bottom waters were hypoxic. It is generally accepted that warmer temperatures (Boszke et al., 2003; Choe and Gill, 2003) and anoxic conditions (Ullrich et al., 2001) stimulate methylation. Based solely on temperature and DO, it could be predicted that August 2004 would have had the highest bottom water MMHg concentrations. Obviously, other factors are controlling methylation and the distribution of bottom water MMHg, allowing for June/July 2004 MMHg concentrations to be 37% greater then in August 2004.

Stratification

The only parameter measured in this study that favors high June/July 2004 bottom water TMMHg concentrations over August 2004 concentrations is the presence of a strong pycnocline in the earlier months. In June/July 2004 the average Brunt-Vaisala frequency for the pycnocline area was 2.32 $1/s^2$ while in August 2004 it was 0.95 $1/s^2$, indicating that water column stratification in June/July 2004 was much stronger then it was in August 2004. Also, in June/July 2004 all but one site was stratified, while only 27% of all sites sampled were stratified in August 2004. This could be the result of an atmospheric front passing over the Gulf of Mexico before the August 2004 cruise, causing wind-induced mixing of the waters and a break down of existing stratification in the Gulf. Weakening of water column stratification as early as August is unusual in the Gulf of Mexico (Rabalais et al., 1994), but serves to highlight the importance of stratification in influencing bottom water TMMHg concentrations.

Stratification in the Gulf could have had such a strong effect on bottom water TMMHg concentrations for two reasons: 1) several researchers have observed that the oxic/anoxic boundary is an area of elevated methylation (Mason et al., 1993; Gagnon et al., 1996). Watras et al. (1995) reported this while studying MMHg in northern Wisconsin lakes. They stated that the oxic/anoxic boundary demonstrated reducing conditions while containing low H_2S concentrations. Gilmour and Henry (1991) also noted that this interface often contained a high particle density, which increases methylation potential. The pycnocline in the Gulf of Mexico often serves as a separation between oxic and hypoxic waters (Rabalais and Turner, 2001), and while it is not a true oxic/anoxic boundary, the difference in oxygen concentrations could enhance water column methylation. It is possible, since bottom water TMMHg concentrations correlate so well with stratification intensity, that the oxic/hypoxic boundary is actually where a substantial portion of the TMMHg is being produced.

Eckley and Hintlemann (2005) found that maximum methylation occurred just below the oxycline in several Canadian lakes, noting that water column methylation might be the source of MMHg to the hypoliminon. Unfortunately, no mid-column MMHg measurements were taken in this study, making it impossible to quantify the amount of MMHg in the pycnocline area.

2) A strong pycnocline could also act as a barrier, preventing bottom water MMHg from diffusing into the entire water column and concentrating MMHg in bottom waters. Canavan et al. (2000) observed a correlation between hypolimnion MMHg concentrations and water column stratification. When stratification began to break down, they noticed that surface water MMHg concentrations increased (Canavan et al., 2000), indicating that stratification had confined MMHg to the hypolimnion. After the water column was fully mixed, surface and bottom water concentrations returned to background levels (Canavan et al., 2000). This is remarkably similar to observations in the Gulf of Mexico, but without mid-column MMHg measurements it cannot be proven.

Sediment

Temporal variability in sediment MMHg followed trends similar to bottom water TMMHg concentrations, implying that water and sediment respond similarly to variations in temperature, oxygen, and other environmental parameters.

MMHg composed a high percent of the THg (average: 8.1 %) in April and June/July 2004, indicating that methylation was taking place in the sediment during this period (Kannan and Falandysz, 1998; Faganelli et al., 2003). Sediment MMHg concentrations also increased during this time, implying that sediment accumulated some of the newly methylated Hg or that the MMHg did not rapidly diffuse out of the sediment. Most studies conducted in other regions indicate that sediment MMHg concentrations increase dramatically during the summer months (e.g. Regnell et al., 1997; Ullrich et al., 2001), so this was expected in the Gulf of Mexico.

By August 2004, MMHg concentrations and MMHg as a percent of THg in surface sediment had decreased but had not been reduced to their minimum values; it is likely that some methylation was still taking place at this time. Sediment MMHg concentrations from June/July to August did not drop as quickly as bottom water concentrations, implying that water column stratification did not influence MMHg in sediment as readily as it influenced bottom water MMHg.

Dissolved Oxygen

The influence of DO on MMHg concentrations is not completely clear on temporal scales, but it becomes more obvious when oxic and hypoxic water and sediment are compared independent of time (Figs. 14, 15). In most instances, lower oxygen environments contained increased MMHg concentrations indicating that oxygen appears to play a role in MMHg production and flux.

In Groups A and C, bottom water concentrations were higher in hypoxic water than in oxic water; in Group B the concentration difference between hypoxic and oxic water was small. These elevated concentrations during low oxygen conditions could be due to increased water column methylation. This would support the hypothesis that methylation in the Gulf is stimulated by hypoxic conditions. The trend could also be explained by an increased MMHg flux from hypoxic sediment into overlying water. Again, this would support the hypothesis that methylation in the Gulf is stimulated by hypoxic conditions.

MMHg concentrations in northern Gulf of Mexico surface sediment are higher during oxic conditions then under hypoxic conditions. Korthals and Winfrey (1987) discovered that surface sediment below oxygenated fresh water had high methylation rates. Similarly, Watras et al. (1995) found that surface sediment below anoxic fresh waters produced low methylation and sulfate reduction rates. Findings from this study correspond well with those studies, but do not support the hypothesis that methylation in the Gulf is stimulated by hypoxic conditions.

Hypoxic sediment in Groups A and C contained MMHg as a higher percent of THg, providing strong evidence that increased methylation in sediment takes place under low oxygen conditions. This was expected since it is generally accepted that anaerobic SRB are mostly responsible for Hg methylation (Compeau and Bartha, 1985; Pak and Bartha, 1998; King et al., 2001). Although findings regarding MMHg concentration and production in the surface sediment are contradictory, MMHg as a percent of THg is generally accepted as a better indicator of methylation than just MMHg concentration because it factors in the total amount of Hg present. Given water concentrations and other factors surrounding this event, it seems likely that sediment below hypoxic waters produced more MMHg than did oxic sediment.

Dissolved oxygen concentrations would most likely control the magnitude of benthic fluxes by dictating the thickness of the oxygenated surface sediment layer (Gagnon et al., 1997; Choe and Gill, 2003). Often this layer is only millimeters thick, but several researchers have noted that MMHg and other metals (e.g. THg) do not easily diffuse through oxic sediment (Gagnon et al., 1997; Choe et al., 2004). This implies that the greatest flux out of the sediment would be when bottom water DO, and therefore the oxygenated sediment layer, was least – in June/July and August 2004.

Fluxes

Taken at face value, benthic flux estimates (Table 2) indicate that, for a majority of the year, MMHg is absorbed into the sediment. However, when coupled with bottom water and surface sediment trends, the data can be put into a different context. These negative fluxes reflect decreases in MMHg concentration in the water column over this time interval. Flux estimates obtained from April to June/July 2004 correspond to a period when bottom water and surface sediment concentrations were already quite high. It is likely that positive fluxes would have been necessary to elevate the MMHg from background wintertime values to the levels observed in April 2004. After this maximum, benthic fluxes steadily decreased for the remainder of the sampling period. It would be reasonable to argue that instead of a flux into the sediment, these negative fluxes simply represent less flux out of the sediment combined with a strong loss process within the water column. As indicated by DO data, it seems likely that the period of highest flux was in June/July and August 2004. If this was the case than benthic fluxes in the Gulf could not have been negative at this time.

Benthic flux estimates in this study took into account very few sites in the hypoxic zone and the calculations involved the use of several large assumptions. Because of this, numbers obtained are probably not representative of fluxes in the entire hypoxic zone at that time. Negative flux values are misleading and likely represent a decrease in flux from the sediment. Despite the shortfalls of these numbers, they do give some insight into bottom water/surface sediment interactions while the water column was stratified. The fluxes estimates in Table 2 should be viewed as indicative of the relative magnitude of sediment-water exchange fluxes for MMHg that can occur in this region of the Texas-Louisana shelf. To put these estimates of benthic flux into perspective, an assessment of atmospheric and riverine fluxes were made for comparison. A description of the approach taken to calculate these fluxes is given in the following sections and is summarized in Table 4.

Rainfall Impact

A three year (2000 – 2003) average of all Gulf of Mexico sites used by the National Atmospheric Deposition Program's Mercury Deposition Network (NADP/MDN) reported an average THg wet deposition of 220 pmol m^{-2} day^{-1} (NADP, 2005). Four studies have been conducted to monitor wet deposition of MMHg in the United States. Despite their wide geographic range, all measurements of MMHg as a percent of THg are in relative agreement. An average of the four studies yields 1.07 ± 0.42 % of THg in the form of MMHg. These values were used to convert the NADP/MDN THg deposition value into a rough MMHg flux of 2.4 pmol m^{-2} day^{-1}.

Mississippi River Input

Surprisingly, there are no published values for MMHg concentrations in the Mississippi River. A concentration of 19.94 pM THg was reported by Garbarino et al. (1995), and a concentration of 0.912 pM MMHg was measured by Krabbenhoft et al (1999) for the Acadian-Pontchartrain basin which is part of the lower Mississippi River basin. An estimate of average freshwater discharge from the Mississippi River was obtained by averaging flow rates recorded by Wiseman et al. (1997), Rabalais et al. (2001), and Wang et al. (2004). Krabbenhoft et al. (1999) published an estimate of 6.78% of THg in the form of MMHg in the Mississippi River basin (Acadian-Pontchartrain) and 3 other river basins emptying into the Gulf of Mexico. From these numbers, a calculated flux of 6.81 - 149 pmol MMHg m^{-2} day^{-1} enters the Gulf (Table 4). Since 67% of this water flows over the hypoxic zone (Rabalais and Turner, 2001), roughly 4.56- 99.8 pmol MMHg m^{-2} day^{-1} enters the hypoxic zone from the Rivers. Balogh et al. (1998) report an estimated THg load of 25 kg/yr at the head of the Mississippi River. This converts to a flux of 1.72 pmol MMHg m^{-2} day^{-1} assuming 6.78% of the Hg is in the form of MMHg and assuming there are no THg inputs into the Mississippi as it flows through the U.S..

Table 4. Flux estimates for MMHg wet deposition and MMHg from the Mississippi River.

Parameter	Measurement	Reference
THg Wet Deposition (3 yr. ave.)	220 pmol m^{-2} day^{-1}	NADP/MDN
% THg as MMHg in Rain	1.50%	Glass and Sorensen (1999)
	0.50%	Mason et al. (2000)
	1.09%	Lawson and Mason (2001)
	1.19%	Hall et al. (2005)
	1.07%	Average of Above
MMHg Wet Deposition for Gulf of Mexico Region	*2.4 pmol m^{-2} day^{-1}*	

Parameter	Measurement	Reference
THg concentration in the Mississippi River	19.94 pM	Garbarino et al. (1995)
	0.912 pM	Krabbenhoft (1999)
THg discharge from the Mississippi River	0.341 mol $year^{-1}$	Balogh et al. (1998)
Mississippi River Discharge	19,000 m^3/s	Wiseman et al. (1997)
	14,000 m^3/s	Rabalais et al. (2001)
	18,400 m^3/s	Wang et al. (2004)
	17,100 m^3/s	Average
% THg as MMHg in the Mississippi River	6.78%	Krabenhoft et al. (1999)
MMHg Discharge from the Mississippi River	*4.56 to 99.8 pmol m^{-2} day^{-1}*	
	1.72 pmol m^{-2} day^{-1}	From Balogh et al. (1998)

Estimated Benthic Flux in the Gulf of Mexico	*-16 to 9.8 pmol m^{-2} day^{-1}*	This Work

The maximum benthic flux estimated by this study was 9.8 pmol MMHg m^{-2} day^{-1}, which is 4 times greater than estimates for MMHg entering the Gulf through wet deposition. The range of possible MMHg input from the Mississippi and Atchafalya Rivers is large, and, although it appears to be greater than MMHg inputs attributed to benthic fluxes, the two estimates are on the same scale. Comparing estimates of benthic MMHg flux to these rough atmospheric and riverine flux estimates, it is clear that, at some times, the sedimentary input of MMHg into the water column is a significant source of MMHg to bottom waters. In fact, during periods of intense stratification, benthic fluxes are the predominant flux to water column of the hypoxic zone. These arguments support the hypothesis that benthic fluxes are an important source of MMHg to the bottom waters of the hypoxic zone.

The magnitude of these fluxes is important because benthic fluxes relocate MMHg from the sediment into the water column where it is more readily incorporated into organisms (Gilmour and Henry, 1991). Fluxes of 9.8 pmol m^{-2} day^{-1} have the potential of releasing 3.95 mol (or 790 g) of MMHg into bottom waters of the hypoxic zone in a month. Obviously, further research will need to be done to refine these numbers, but benthic fluxes could represent a major pathway of MMHg entering the Gulf of Mexico food web.

Temperature

The relationship found between bottom water temperature and MMHg concentrations is opposite of hypothesized trends. Ordinarily temperature and MMHg concentration are directly related (Korthals and Winfrey, 1987; Boszke et al., 2003), while this study found them to be almost inversely correlated. A similar phenomenon was observed in the Gulf of Trieste: maximum benthic fluxes and bottom water concentrations were observed in autumn when bottom water DO and temperature were in the middle of their range (Covelli et al., 1999). Covelli et al. (1999) explained that this transitional phase was ideal for methylation and MMHg accumulation due to a change in the nature of sulfide-Hg interactions. Though possible in the Gulf of Mexico, sulfide measurements would be needed to support this explanation. There are several other explanations that could explain this trend. It is possible that, in the Gulf of Mexico, temperature is not a large factor controlling methylation. This might also indicate that summer bottom water temperatures (reaching a maximum of 28.2ºC) were warm enough to inhibit bacterial methylation. It is also possible that warmer temperatures increased bioirrigation in the surface sediment (Schluter et al., 2000). Worms and other benthic invertebrates were found in some cores collected from the hypoxic zone, making this explanation feasible, although low oxygen concentrations may limit this to a minor factor.

Spatial Variability

By sampling at a fine resolution, Eckley and Hintlemann (2005) found small regions of increased methylation that could have been overlooked if they had been sampling at larger intervals. It is possible that in the Gulf of Mexcio some of those small regions were serendipitously sampled and are represented by the elevated concentrations recorded at sites 12A in April 2004 and 07A in June/July 2004. If this is true, than many more areas in the Gulf have the potential to produce similarly high MMHg concentrations.

Sites 12A and 07A may seem anomalous in this data set, but they share several characteristics that are worth discussing. Both sites had high Brunt-Vaisala frequencies when compared with other Gulf sites: 3.35 $1/s^2$ at 07A and 3.19 $1/s^2$ at 12A. Other sites sharing high Brunt-Vaisala frequencies (> 2.5 $1/s^2$) also had elevated MMHg concentrations. Again, this emphasizes the correlation between stratification and total MMHg concentrations. (Table 5 contains more information on these sites.)

Sites sharing commonalities with the two anomalous sites are also all in Group A. There are two reasons why sites in Group A would experience elevated MMHg concentrations. Group A sites - including sites 12A and 07A - showed decreases in salinity in April and June/July 2004 caused by freshwater input from the Mississippi River. This would explain the higher degrees of stratification in Group A during this time (ave.: 2.75 $1/s^2$) and the resulting increase in MMHg. It is also possible, since the Mississippi discharges roughly 0.075 – 4.31 pmol MMHg m^{-3} day^{-1} into the hypoxic zone, that a majority of this MMHg is deposited in Group A. It is likely that both scenarios play a role in the increased concentrations of this area.

Monomethylmercury concentrations in the surface sediment of Group A were also greater than in other groups. The Mississippi River probably contributed to these increased concentrations as well. The River carries 1.5 x 10^5 kg/day of suspended sediment to the Gulf (Meade, 1995). At a site (28°55.48N and 89°40.63W) slightly south of Group A, a sedimentation rate of 0.7 cm/yr was measured (Oktay et al., 1999). Given this, it is likely that suspended sediment and sedimentation played a role in increasing MMHg concentrations in the benthos of Group A.

Table 5. Brunt-Viasala frequencies, TMMHg concentrations, and surface salinities for select sites in Group A.

Site	Date	Brunt-Vaisala Frequency (N^2)	[TMMHg] (pM)	Surface Salinity
12A	April 2004	3.19	0.150	25.5
7A	June/July 2004	3.35	0.329	18.7
16A	June/July 2004	4.32	0.055	15.6
12A	March 2005	2.84	0.035	20.5
11A	May 2005	2.70	0.036	20.1

Bottom water temperatures for Group A stayed much cooler during June/July and August 2004 than both other groups – 6.3º cooler than Group B, and 5.5º cooler than Group C. The cause of this is unknown, but if high temperatures did inhibit methylation, then this could also be the reason TMMHg concentrations in Group A were elevated when compared to other groups.

Groups A, B, and C all exhibited by slightly different environmental conditions which is one explanation for the difference in TMMHg concentrations observed in these areas. These differences make clear that the hypoxic zone cannot be looked at as a homogenous area of MMHg production.

Comparison

Compared to MMHg concentrations in ocean basins elsewhere in the world, the Gulf of Mexico has a relatively low concentration of MMHg in bottom water (Table 6). Most other marine sites that have been examined have a greater freshwater influence or were Hg-contaminated sites, so this is not surprising.

Sediment MMHg concentrations in the Gulf of Mexico were similar to concentrations found in near-by drainage basins; the summer and fall Gulf of Mexico average of 1.83 ± 1.85 pmol/g MMHg was similar to those reported by Krabbenhoft et al. (1999) for the Acadian-Pontchartrain Basin, the Mobile River, and Trinity River Basin. Summer MMHg and THg concentrations in Gulf surface sediment (MMHg: 1.86 ± 1.86 pmol/g, THg: 159.2 ± 102.9) were similar to concentrations reported by Trefry et al. (2002) for three Gulf of Mexico sites studied in May 2002 (MMHg: 2.19 ± 1.35 pmol/g, THg: 54.8 – 458.7 pmol/g). Background concentrations in deeper sediments (8-10 cm) were also similar to those reported by Trefry et al. (2002); they reported MMHg and THg concentrations of 0.66 ± 0.53 pmol/g and 207.9 ± 145.07 pmol/g, respectively, while concentrations determined in this project were 0.975 ± 0.502 pmol/g and 178 ± 98.3 pmol/g, respectively.

Table 6. MMHg concentrations in water and MMHg concentrations and total Hg concentrations in sediment at various locations. All sediment concentrations are in pmol/g, all water concentrations are in pM.

Location	Media	Collection Date	Concentration	Comments	Reference
Gulf of Mexico: 29°15N, 88°46W 29°14N, 88°24W 28°09N, 91°22W	Sediment (0-1 cm)	May	MMHg: 2.19 ± 1.35 THg: 54.8-458.7	Eastern Section of 'Group A'	Trefry et al.(2002)
Bays and Harbors on West Florida Coast	Sediment (0-2 cm)	June	MMHg: .005 – 2.44 THg: 4.99 – 1091		Kannan et al. (1998)
Lavaca Bay, TX	Sediment (0-1 cm)	Spring Winter	MMHg: 32.01 THg: 3769 MMHg: 8.33 THg: 2393	Heavily Contaminated Site	Bloom et al. (1999)
Long Island Sound	Sediment (0-4 cm)	March June August	MMHg: 7.83 THg: 982.1 MMHg: 6.63 THg: 867.4 MMHg: 6.93 THg: 1027		Hammerschmidt and Fitzgerald (2004)
Southern Baltic Sea	Sediment (0-5 cm) Water	September	THg: 10 - 1700 MMHg <0.13 - 4.68	Permanently Anoxic, Salinity ~8 - 17 PSU	Pempkowiak et al. (1998)
Acadian-Pontchartrain Basin Mobile River and Tributaries Southern Florida Trinity River Basin	Sediment , Water	June - October	MMHg: 1.10 , 0.91 MMHg: 1.19 , 0.33 MMHg: 25.18 , 2.19 MMHg: 1.37 , 0.12	Freshwater	Krabbenhoft et al. (1999)
Gulf of Trieste	Water	September	MMHg: 0.02 - .31	Seasonally Stratified Old Cinnabar Mine	Covelli et al. (1999)
Gulf of Trieste	Water	March June August September	MMHg: 0.12 – 0.18 MMHg: <.12 – 0.39 MMHg: 0.35 – 0.63 MMHg: <0.12		Faganeli et al. (2003)
Scheldt Estuary in the Southern North Sea	Water	Feburary June/July August October December	MMHg: 1.35 MMHg: 0.781 MMHg: 2.34 MMHg: 0.555 MMHg: 0.21	Salinity Range: ~ 0 - 30 PSU	Leermakers et al. (2001)

CONCLUSION

Many studies have been conducted in stratified, seasonally anoxic lakes, but significantly fewer studies have been conducted in stratified, seasonally anoxic marine waters. Areas such as the Gulf of Trieste (Covelli et al., 1999; Horvat et al., 1999) have been well studied, and there have been initial studies conducted in the North (Leermakers et al., 2001) and Baltic (Pempkowiak et al., 1998) Seas. Although there are similarities between the Gulf of Mexico and some of these sites, the Gulf of Mexico also proves to be unique in several different ways.

Stratification intensity plays a major role in controlling MMHg concentrations in the bottom water on the northern Gulf of Mexico shelf. Because this study did not sample MMHg in the entire water column, it remains unclear how exactly stratification effects MMHg concentration, but the strong correlation between the two warrants further study.

Dissolved oxygen and temperature also play a role controlling MMHg concentrations in bottom water and surface sediment. Contrary to most published literature, peak methylation in the shelf waters of the northern Gulf of Mexico occurs when DO and temperature are in the middle of their range. During this study, this occurred in June/July 2004 when DO was 1.81 mL/L and bottom water temperature was 23.89°C. Both DO and temperature seem to be inversely related to bottom water TMMHg concentrations. Although this is a typical finding for DO-MMHg interactions, it is unusual to find this type of relationship describing temperature and MMHg. A possible explanation is that summer increases in water temperature inhibit bacterial methylation; more work should be done to further characterize these relationships.

MMHg fluxes out of the sediment also seemed to impact bottom water TMMHg concentrations. Measurements of benthic fluxes are approximations, but give a good idea of magnitude. Maximum benthic fluxes were roughly 4 times more then MMHg concentrations in wet deposition, and on roughly the same scale as inputs from the Mississippi River. Calculations were made as MMHg diffusion decreased from the sediment; further research should be conducted to capture a full year cycle in better resolution.

In some instances, Group B trends relating MMHg to oxygen concentrations were unique when compared to the other two groups. It was thought that water and sediment would respond similarly to low oxygen conditions throughout the Gulf, which was clearly not the case. Water and sediment in Group B responded differently to low DO than other groups. This could be because Group B was the only group studied without a strong riverine influence.

Groups A, B, and C within the hypoxic zone are controlled by slightly different environmental conditions, resulting in different TMMHg concentrations in both the water and sediment of the three groups. Spatial variation is great enough that the hypoxic zone cannot be looked at as a homogenous area of MMHg production. The best example of this is Group A – the group closest to the Mississippi River – which had the widest range of MMHg concentrations. It appears these higher concentrations are partially due to the influence of Mississippi River discharge, but could also be due to other parameters such as temperature or stratification. Again, further research in this area and MMHg concentrations in the Mississippi River delta would be needed to determine why Group A was dissimilar to other areas sampled.

There are also significant yearly variations in the timing of MMHg production in this area. This is most likely related to the timing of stratification and hypoxia formation, but annual surveys would need to be conducted to confirm this.

This study has left many questions unanswered, but has given us a glimpse into the behavior of MMHg in the Gulf of Mexico and of the environmental parameters that help control its production. MMHg concentrations in Gulf of Mexico fish are high because the food web is exposed to elevated levels of MMHg; until a source and solution have been found for this problem we should continue to monitor Hg in the Gulf closely.

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APPENDIX

Table 7. Hypoxic bottom water TMMHg, PMMHg, and CTD measurements taken from April 2004 - May 2005. CTD measurements for August 2004 site 07A were not recorded, data listed are for closest site.

Site	Month	Depth (m)	Temp (c)	DO (mL/L)	Salinity (PSU)	Particles (mg/L)	PAR (µE/m2/s)	TMMHg (pM)	TMMHg SD (pM)	PMMHg (pM)	PMMHg SD (pM)
07A	Jun-04	8.5	27.900	1.4	34.680	3.4		0.3290	0.0734	--	
MOOR-12B	Jun-04	16.5	27.250	1.0	35.956	3.8	2.460	0.0249		--	0.0301
02A	Aug-04	19	25.9	.934	35.8	7.500		0.0598		0.0548	
07AC(B)	Aug-04	*16*	*26.9*	*1.341*	*35.5*	*4.125*	*3.36*	0.0150	0.0301	0.0150	
16A	Aug-04	56	21.1	1.200	36.4	4.877		0.0399		0.0199	0.0256
10B	Aug-04	20	28.7	1.171	35.1	2.638		0.0199		0.0100	
07C	Aug-04	9.5	28.2	.953	30.6	7.500		0.0947		0.0847	0.0239
10C	Aug-04	31	24.2	.513	35.8	4.221	23.16	0.0100			
16C	Aug-04	19.5	26.4	1.105	35.4	2.431	5.60	0.0199	0.0239	0.0050	0.0261
07A	Mar-05	9.5	20.4	.962	34.6	7.119		0.0199	0.0162	-0.0100	
07A	May-05	11	22.5	.108	34.7	2.976	2.24	0.0255		-0.0008	
11A	May-05	11	24.4	.676	35.8	6.747	3.93	0.0358	0.0306	0.0160	

Table 8. Oxic bottom water TMMHg, PMMHg, and CTD measurements taken from April 2004 - May 2005.

Site	Month	Depth (m)	Temp (c)	DO (mL/L)	Salinity (PSU)	Particles (mg/L)	PAR (µE/m2/s)	TMMHg (pM)	TMMHg SD (pM)	PMMHg (pM)	PMMHg SD (pM)
12A	Apr-04	22.5	21.10	3.57	36.3	0.81	5.07	0.1496		--	
MOOR-12B	Apr-04	19.0	21.32	3.75	36.1	6.65	246.20	0.0349		--	
08C	Apr-04	19.5	20.76	4.13	35.7	5.93	22.14	0.0349		--	

Table 8 (Continued).

Site	Month	Depth (m)	Temp (c)	DO (mL/L)	Salinity (PSU)	Particles (mg/L)	PAR (µE/m2/s)	TMMHg (pM)	TMMHg SD (pM)	PMMHg (pM)	PMMHg SD (pM)
10A	Jun-04	59.5	20.10	2.33	36.4	6.44		0.0698		--	
12A	Jun-04	30.0	21.70	1.90	36.4	5.40	2.46	0.0449		--	
16A	Jun-04	56.5	20.35	2.66	36.4	4.53	2.46	0.0548		--	
16C	Jun-04	21.5	26.02	1.62	35.3	7.99	19.29	0.0399		--	
10A	Aug-04	58.5	20.73	1.47	36.4	5.91	2.46	0.0349	0.0316	0.0299	
12A	Aug-04	38	24.11	1.80	36.3	7.45		0.0349	0.0120	0.0199	0.0120
07B	Aug-04	9.5	28.51	1.79	30.2	2.84	7.74	0.0399		0.0199	
MOOR-12B	Aug-04	17.5	28.39	1.51	34.6	3.72	2.46	0.0499	0.0342	0.0199	0.0342
18B	Aug-04	20	26.77	2.37	35.7	3.14	2.46	0.0199	0.0184	0.0150	
08C	Aug-04	19	28.18	1.52	33.4	3.03	2.44	0.0150		0.0050	
C4	Oct-04	12.4	27.01		34.9			0.0000		0.0050	
C5	Oct-04	15.8	27.08		35.0			0.0100	0.0204	--	
C6C	Oct-04	18.9	27.20		35.2			0.0199		0.0100	
C8	Oct-04	24.3	27.51		35.9			0.0100		0.0199	
C9	Oct-04	30	27.20		36.1			0.0399		0.0299	
02A	Mar-05	20	20.95	1.75	35.8	7.50		0.0499		-0.0050	
12A	Mar-05	19.5	20.94	2.68	36.0	4.64		0.0349	0.0141	0.0100	0.0344
10B	Mar-05	21.5	20.71	2.85	35.8	5.47		0.0299		0.0249	
12B	Mar-05	20	20.82	1.96	35.8	7.38		0.0598		-0.0947	0.0856
17B	Mar-05	18.5	20.79	1.95	36.0	7.50		0.0100		-0.0050	
02C	Mar-05	20	20.09	2.88	35.4	7.51		0.0150		-0.0199	0.0266
08C	Mar-05	18.5	20.07	2.67	35.0	5.91		0.0150		-0.0100	
16C	Mar-05	20.5	20.30	2.44	35.5	5.47		0.0349		0.0100	
02A	May-05	19	23.75	1.99	35.9	6.10	12.40	0.0353		0.0022	0.0515
12A	May-05	20.5	23.66	2.81	36.3	6.47	0.94	0.0101		0.0042	0.0216
10B	May-05	21.5	21.92	2.48	36.2	3.50	15.20	0.0173		-0.0041	0.0193
12B	May-05	19	23.26	3.29	36.1	3.35	0.67	0.0279		-0.0132	0.0410
02C	May-05	20.5	21.31	2.24	35.9	2.54	28.20	0.0062		-0.0275	
08C	May-05	21	21.63	2.59	35.7	4.46	1.87	0.0531	0.0360	0.0275	0.0360
16C	May-05	20	20.84	2.46	36.2	4.20	6.81	0.0032		0.0039	

Table 9. Surface water TMMHg, PMMHg, and CTD measurements taken from April 2004 - May 2005. CTD measurements for August 2004 site 07A were not recorded, data listed are for closest site.

Site	Month	Depth (m)	Temp (c)	DO (mL/L)	Salinity (PSU)	Particles (mg/L)	PAR (µE/m2/s)	TMMHg (pM)	TMMHg SD (pM)	PMMHg (pM)	PMMHg SD (pM)
12A	Apr-04	2.0	21.11	6.65	25.5	1.07	1299	0.0399		--	
MOOR-12B	Apr-04	2.0	21.51	4.78	34.2	0.04	1780	0.0249		--	
08C	Apr-04	2.0	21.75	5.70	28.0	0.68	1144	0.0199			
07A	Jun-04	2.5	29.76	4.07	18.7	5.41		0.0299			
10A	Jun-04	3.0	29.62	3.31	29.5	3.60		0.0399			
12A	Jun-04	2.5	29.88	3.31	19.4	6.78	96.3	0.0499			
16A	Jun-04	2.5	28.79	2.61	15.6	7.50	70.1	0.0100			
16C	Jun-04	2.0	29.15	3.23	30.6	2.11	782.4	0.0199			
02A	Aug-04	1.5	29.10	3.81	26.7	2.88		0.0299	0.0163	0.0199	
07A	Aug-04	2	29.12	4.01	27.4	2.72	1349.0	0.0349	0.0101	0.0150	0.0172
10A	Aug-04	2	28.95	3.87	26.3	2.68	134.9	0.0249	0.0218	0.0100	0.0218
12A	Aug-04	1.5	29.96	4.24	26.8	2.73		0.0150	0.0034		0.0091
16A	Aug-04	2	29.85	4.22	26.0	2.68		0.0050	0.0093		0.0093
07B	Aug-04	2	29.12	3.35	27.7	3.46	221.4	0.0349		0.0199	
10B	Aug-04	2	29.54	3.19	30.4	2.20		0.0150		0.0100	0.0210
MOOR-12B	Aug-04	2	29.62	3.41	27.8	2.44	1087.0	0.0100	0.0064	0.0050	0.0091
18B	Aug-04	2	29.68	3.09	28.8	2.31	23.5	0.0100		0.0100	
07C	Aug-04	2	29.39	3.11	26.9	2.56		0.0499	0.0177	0.0449	
08C	Aug-04	2	28.76	2.92	29.2	2.24	80.1	0.0100		0.0050	
10C	Aug-04	2	29.72	2.97	33.5	2.08	1374.0	0.0100			
16C	Aug-04	1.5	29.55	3.01	31.7	2.30	72.0	0.0199	0.0189	0.0100	0.0189
C4	Oct-04	0.4	27.37		27.7			0.0000			
C5	Oct-04	0.3	27.60		27.4			0.0299			
C6C	Oct-04	0.1	28.01		14.0			0.0150			
C8	Oct-04	0.7	26.86		27.9			0.0199		0.0050	
C9	Oct-04	0.4	26.82		28.0			0.0100		0.0050	
02A	Mar-05	2	20.97	7.30	20.2	3.92		0.0199	0.0196	0.0050	0.0204
07A	Mar-05	1.5	20.90	6.41	22.7	3.25		0.0249			
12A	Mar-05	1	20.58	6.81	20.5	4.22		0.0249	0.0195	-0.0100	

Table 9 (Continued).

Site	Month	Depth (m)	Temp (c)	DO (mL/L)	Salinity (PSU)	Particles (mg/L)	PAR (µE/m2/s)	TMMHg (pM)	TMMHg SD (pM)	PMMHg (pM)	PMMHg SD (pM)
10B	Mar-05	2	20.93	4.97	31.9	2.26		0.0249	0.0167	0.0150	0.0167
12B	Mar-05	1.5	20.37	6.58	24.7	3.19		0.0100		-0.0050	0.0207
17B	Mar-05	2	20.76	5.75	26.5	3.12		0.0100	0.0143		0.0143
02C	Mar-05	1.5	19.20	6.69	24.8	3.40		0.0100	0.0266		
08C	Mar-05	1.5	18.87	6.96	21.2	5.15		0.0349	0.0114	0.0349	
16C	Mar-05	2	19.40	6.05	27.7	3.08		0.0150			
02A	May-05	1.5	28.59	4.95	21.7	1.79	1900.0	0.0129		-0.0082	0.0125
07A	May-05	2	27.93	5.22	19.9	1.75	91.6	0.0164		0.0013	0.0073
11A	May-05	2	27.89	5.02	20.1	1.70	145.0	0.0364		0.0247	
12A	May-05	2	28.00	6.04	19.8	2.97	261.0	0.0349	0.0216	0.0163	
10B	May-05	2	27.93	4.88	23.8	1.90	438.0	0.0113		0.0034	0.0088
12B	May-05	1.5	28.25	4.83	26.9	2.23	50.9	0.0189	0.0164	0.0128	0.0164
02C	May-05	1.5	26.27	4.12	29.3	1.32	469.0	0.0110		-0.0061	
08C	May-05	2	25.99	4.15	28.5	1.33	121.0			-0.0114	
16C	May-05	1.5	26.81	4.02	28.7	1.29	209.0	0.0076		0.0019	

Table 10. Sediment MMHg concentrations, total Hg concentrations, and MMHg:THg ratios for individual sites.

Depth (cm)	12A MMHg	12A THg	12A Ratio	12B MMHg	12B THg	12B Ratio	08C MMHg	08C THg	08C Ratio
Month	Apr-04	Apr-04	Apr-04	Apr-04	Apr-04	Apr-04	Apr-04	Apr-04	Apr-04
0-1	2.622	246.916	5.295	3.732	154.607	12.034	4.524	177.417	12.712
1-2	1.625	258.907	3.129	2.173	173.249	6.252	2.632	179.603	7.306
2-3	0.973	257.336	1.884	1.089	166.124	3.269	3.257	175.173	9.269
3-4	1.408	304.449	2.306	0.661	52.316	6.294	2.154	154.627	6.945
4-5	1.867	512.605	1.816	0.864	70.585	6.104	1.543	157.205	4.894
5-6	1.212	486.616	1.242	1.055	82.139	6.401	1.867	207.116	4.494
6-7	1.649	333.355	2.467	0.823	111.335	3.686	2.411	204.651	5.873
7-8	2.262			0.627	120.032	2.604	2.536	100.389	12.592
8-9	1.028						1.796	59.687	14.998
9-10	1.279						1.526	184.288	4.128

Depth (cm)	10A MMHg	10A THg	10A Ratio	12A MMHg	12A THg	12A Ratio	16A MMHg	16A THg	16A Ratio
Month	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04
0-1	10.508	344.718	15.197	8.220	269.525	15.204	3.916	395.370	4.938
1-2	7.911	257.103	15.340	2.393	403.319	2.958	3.901	330.169	5.890
2-3	3.873			2.441	479.383	2.538	2.182		
3-4	3.589			1.974	296.189	3.323	1.279		
4-5	3.910			2.566	312.111	4.098	1.498		
5-6	4.030			1.218	350.655	1.732	2.182		
6-7	4.032			1.099			1.299		
7-8	4.114			1.196			1.146		
8-9	3.234			0.870			1.179		
9-10	3.247			1.066			1.681		

Table 10 (Continued).

Depth (cm)	16A MMHg (dup)	16A THg (dup)	16A (dup) Ratio	12B MMHg	12B THg	12B Ratio	02A MMHg	02A THg	02A Ratio
0-1	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04	Jun-04	Aug-04	Aug-04	Aug-04
1-2	4.123	172.800	11.895	1.757	280.591	3.122	4.179	200.361	10.397
2-3	4.865	198.827	12.199	1.959	256.263	3.812	3.256	205.854	7.884
3-4	3.118			1.549	275.783	2.800	2.826		
4-5	1.970			1.951	387.598	2.509	2.215		
5-6	1.937			1.414	264.361	2.667	1.957		
6-7	1.803			0.380	69.107	2.739	2.568		
7-8	1.394			0.740	180.026	2.050	1.404		
8-9	1.361			0.332	111.013	1.490	1.652		
9-10	1.265			0.171	177.314	0.479	0.557		
0-1	1.190			1.107	132.722	4.158	0.517		

Depth (cm)	07A MMHg	07A THg	07A Ratio	10A MMHg	10A THg	10A Ratio	12A MMHg	12A THg	12A Ratio
Month	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04
0-1	1.442	172.229	3.533	3.234	203.483	7.924	1.837	492.283	1.860
1-2	1.002	128.927	2.289	3.066	218.239	7.004	1.479	270.917	2.722
2-3	0.669			2.952			0.851	235.457	1.802
3-4	0.794			4.177			0.716	287.439	1.242
4-5	0.520			1.943			0.831	305.159	1.358
5-6	0.446			3.219			0.814	266.957	1.520
6-7	1.124			3.193			1.152	330.130	1.740
7-8	0.381			3.205			0.834	154.125	2.699
8-9	0.323			3.512			0.900	249.637	1.796
9-10	0.171			3.145			0.866	298.481	1.446

Table 10 (Continued).

Depth (cm)	16A MMHg	16A THg	16A Ratio	07B	07B THg	07B Ratio	10B MMHg	10B THg	10B Ratio
Month	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04
0-1	1.716	88.111	9.707	4.695	163.071	14.352	0.764	62.805	6.067
1-2	1.319	167.003	3.937	2.808	149.406	9.370	0.781	57.273	6.796
2-3	1.375			1.206			0.959		
3-4	1.553			0.800			1.037		
4-5	1.035			0.550			1.099		
5-6	1.071			0.673			1.062		
6-7	1.161								
7-8	0.657								
8-9	0.872								
9-10	0.965								

Depth (cm)	12B MMHg	12B THg	12B Ratio	18B	18B THg	18B Ratio	07C	07C THg	07C Ratio
Month	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04
0-1	3.404	233.066	7.280	0.490	28.153	8.681	1.400	59.251	11.781
1-2	2.767	234.843	5.874	0.320	27.530	5.800	0.866	57.790	7.470
2-3	1.555	245.396	3.158	0.789			1.490		
3-4	1.075	229.358	2.336	0.878			1.199		
4-5	0.612	133.324	2.287	0.585			1.307		
5-6	0.239	51.538	2.312	0.748			1.127		

Table 10 (Continued).

Depth (cm)	08C MMHg	08C THg	08C Ratio	10C MMHg	10C THg	10C Ratio	16C MMHg	16C THg	16C Ratio
Month	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04	Aug-04
0-1	1.252	238.933	2.612	0.770	101.354	3.786	1.551	136.334	5.673
1-2	1.231	181.199	3.387	0.977	86.962	5.600	1.289	133.725	4.807
2-3	0.841	183.933	2.280	0.941			1.327		
3-4	0.775	186.415	2.072	0.749			1.063		
4-5	0.580	166.785	1.734	0.765			0.580		
5-6		190.441		0.577			0.472		
6-7		138.696							
7-8		164.671							

Depth (cm)	C6C MMHg	C6C THg	C6C Ratio	02A MMHg	2A THg	2A Ratio	12A MMHg	12A THg	12A Ratio
Month	Oct-04	Oct-04	Oct-04	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05
0-1	0.856	144.694	2.950	0.886	212.964	2.074	0.882	193.479	2.274
1-2	0.823	166.185	2.470	1.917	178.912	5.341	1.018	228.052	2.226
2-3	0.709			1.901			0.980	271.374	1.799
3-4	0.892			2.313			1.006	219.523	2.285
4-5	0.517			1.889			0.921	247.018	1.858
5-6	0.688			1.544			0.859	246.696	1.737
6-7								247.879	
7-8								209.937	
8-9								263.271	
9-10								247.333	

Table 10 (Continued).

Depth (cm)	02A MMHg	2A THg	2A Ratio	12A MMHg	12ATHg	12A Ratio	10B MMHg	10B THg	10B Ratio
Month	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05
0-1	0.886	212.964	2.074	0.882	193.479	2.274	0.385	32.917	5.826
1-2	1.917	178.912	5.341	1.018	228.052	2.226	0.524	34.308	7.616
2-3	1.901			0.980	271.374	1.799	0.462		
3-4	2.313			1.006	219.523	2.285	0.958		
4-5	1.889			0.921	247.018	1.858	1.145		
5-6	1.544			0.859	246.696	1.737	0.868		
6-7					247.879				
7-8					209.937				
8-9					263.271				
9-10					247.333				

Depth (cm)	10B MMHg	10B THg	10B Ratio	12B MMHg	12B THg	12B Ratio	12B (dup) MMHg	12B (dup) THg	12B (dup) Ratio
Month	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05
0-1	0.385	32.917	5.826	2.480	235.173	5.258	1.134	109.535	5.160
1-2	0.524	34.308	7.616	1.303	201.816	3.218	0.622	115.914	2.676
2-3	0.462			0.958	194.987	2.449	0.544		
3-4	0.958			0.747	242.341	1.537	1.169		
4-5	1.145			0.464	240.243	0.964	0.306		
5-6	0.868			1.838	300.427	3.049			
6-7					198.414				
7-8					199.520				
8-9					179.979				
9-10					173.982				

Table 10 (Continued).

Depth (cm)	17A MMHg	17A THg	17A Ratio	17A (dup) MMHg	17A (dup) THg	17A (dup) Ratio	02C MMHg	02C THg	02C Ratio
Month	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05
0-1	0.604	135.255	2.225	0.524	166.050	1.572	1.211	73.332	8.234
1-2	0.795	145.052	2.731	0.481	104.751	2.288	0.893	79.166	5.624
2-3	1.058			0.442			0.875		
3-4	0.437			0.969			1.028		
4-5	0.428						1.125		
5-6	0.483						1.673		

Depth (cm)	08C MMHg	08C THg	08C Ratio	08C (dup) MMHg	08C (dup) THg	8C (dup) Ratio	16C MMHg	16C THg	16C Ratio
Month	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05	Mar-05
0-1	1.211	152.385	3.963	1.008	118.994	4.225	0.636	115.392	2.749
1-2	0.893	156.623	2.842	1.486	152.230	4.867	0.779	97.795	3.970
2-3	0.875	165.744	2.633	2.787	349.593	3.975	0.929		
3-4	1.028	158.668	3.229	0.877	165.625	2.640	0.933		
4-5	1.125	167.864	3.340	1.159	168.160	3.435	0.745		
5-6	1.673	175.569	4.750		226.346		0.668		
6-7		165.396							
7-8		172.327							
8-9		176.087							
9-10		135.807							

Table 10 (Continued).

Depth (cm)	02A MMHg	02A THg	02A Ratio	11A MMHg	11A THg	11A Ratio	12A MMHg	12A THg	12A Ratio
Month	May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05
0-1	2.756	190.329	7.218	1.773	133.347	6.627	1.096	272.206	2.007
1-2	2.658	217.996	6.079	1.894	182.149	5.183	0.820	244.841	1.670
2-3	1.933			1.443			1.178	0.000	0.000
3-4	2.309			1.042			1.066	95.100	5.589
4-5	1.791			2.365			0.876	46.042	9.480
5-6	1.501						1.066	26.732	19.883

Depth (cm)	12A (dup) MMHg	12A (dup) THg	12A (dup) Ratio	10B MMHg	10B THg	10B Ratio	12B MMHg	12B THg	12B Ratio
Month	May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05
0-1	0.605	289.900	1.040	0.540	31.679	8.501	0.720	95.100	3.773
1-2	1.016	296.181	1.710	1.103	46.610	11.802	0.500	46.042	5.413
2-3	1.172	0.000	0.000	1.308			0.370	26.732	6.899
3-4	0.000	95.100	0.000	0.973			0.440	24.495	8.964
4-5	1.108	46.042	12.000	0.785			0.464	20.420	11.331
5-6		26.732		0.593			0.671	68.134	4.910
6-7								93.664	
7-8								244.348	
8-9								145.639	
9-10								185.998	

Table 10 (Continued).

Depth (cm)	12B (dup) MMHg	12B (dup) THg	12B (dup) Ratio	02C MMHg	02C THg	02C Ratio	08C MMHg	08C THg	08C Ratio
Month	May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05
0-1	0.631	67.740	4.643	0.635	82.400	3.841	0.727	148.442	2.440
1-2	0.395	34.526	5.705	0.493	49.306	4.982	0.664	180.935	1.829
2-3	0.282			0.454			1.201	196.221	3.051
3-4	0.220			0.356			1.147	180.437	3.169
4-5	0.274			0.430			1.146	169.537	3.371
5-6							1.389	157.299	4.403
6-7								162.840	
7-8								184.842	

Depth (cm)	08C (dup) MMHg	08C (dup) THg	08C Ratio	16CC MMHg	16C THg	16C Ratio
Month	May-05	May-05	May-05	May-05	May-05	May-05
0-1	1.101	120.294	4.564	1.171	119.004	4.905
1-2	0.957	82.494	5.781	1.622	105.410	7.672
2-3	1.870			1.254		
3-4	0.645			1.262		
4-5	1.267			0.373		

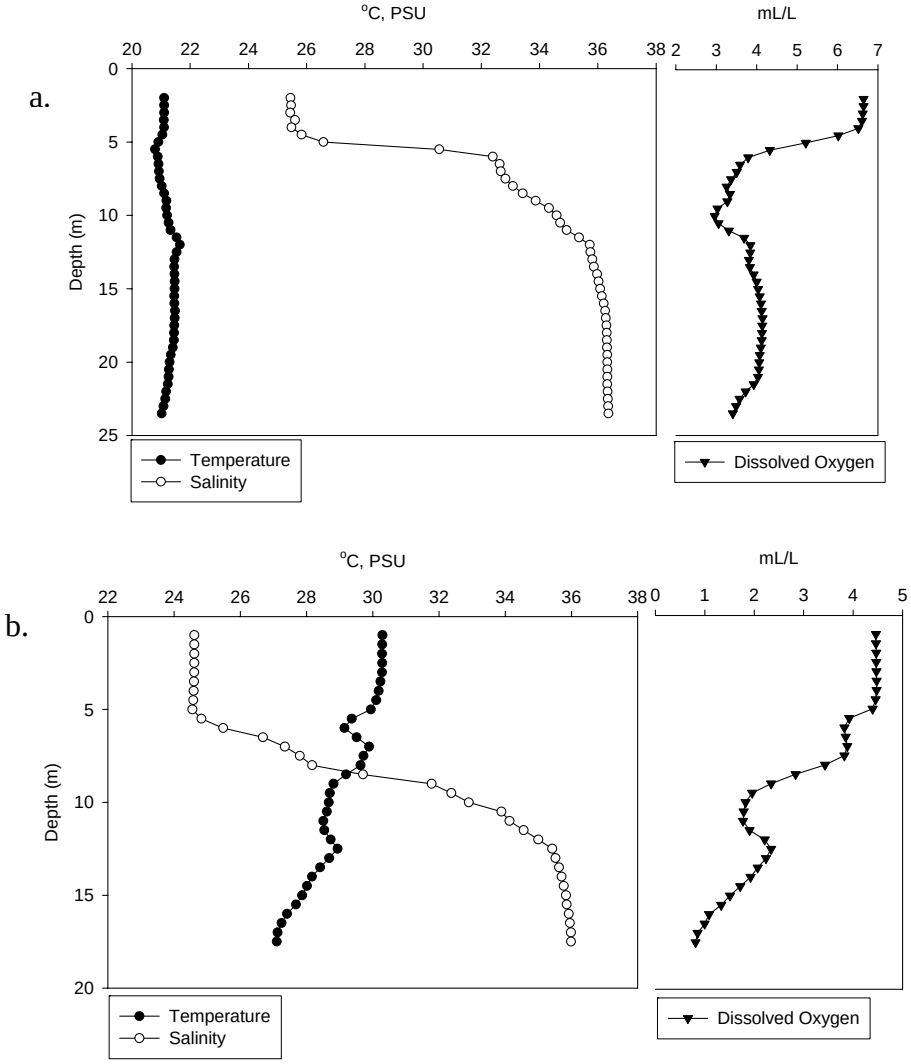


Fig. 18. Temperature, salinity, and DO water profiles taken by the CTD. Sites displayed were selected because they are representative of conditions in the Gulf of Mexico during those months. A DO profile was not included for October 2004 because the DO meter was incorrectly calibrated. Profile A was taken in April 2004 at site 12A, profile B was recorded at site 12B in June/July 2004. In August 2004, profile C was recorded at site 10B. Profile D was taken in October 2004 at site C6C. Profiles E and F were recorded during cruises in March and May 2005 at sites 12B and 07A, respectively.

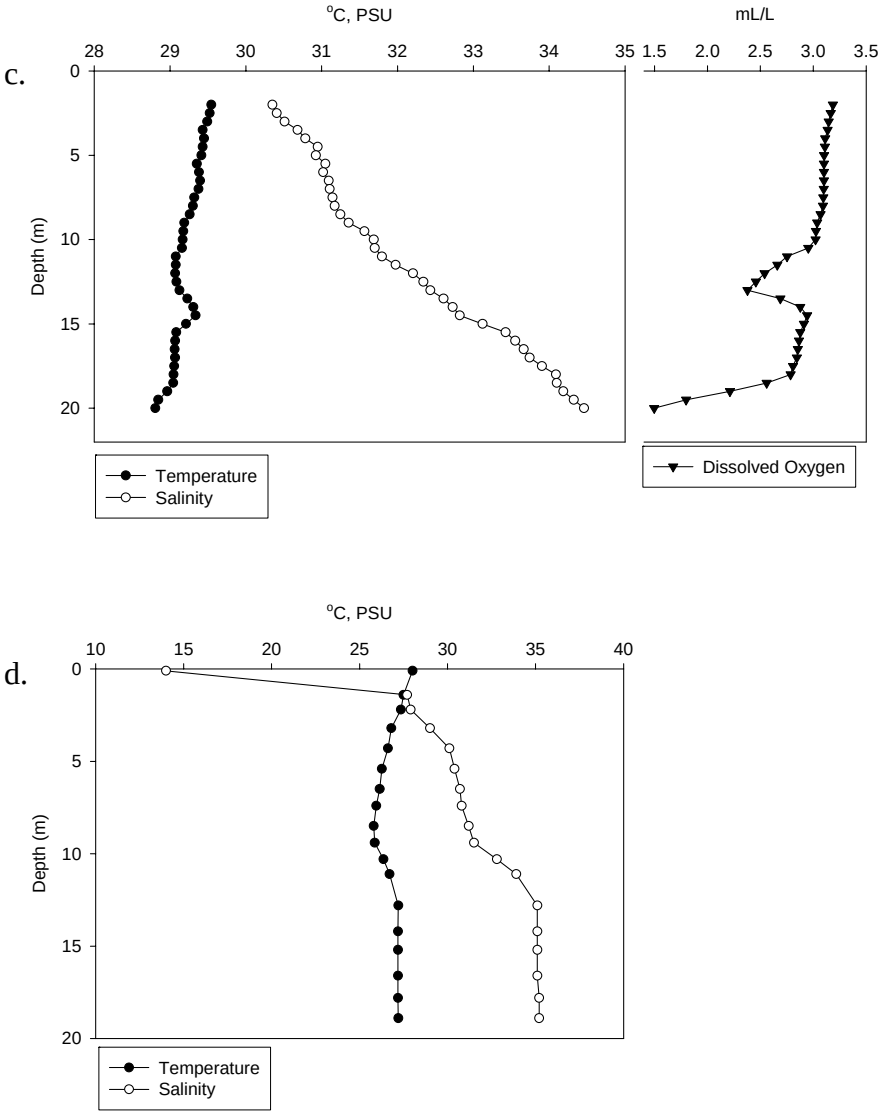
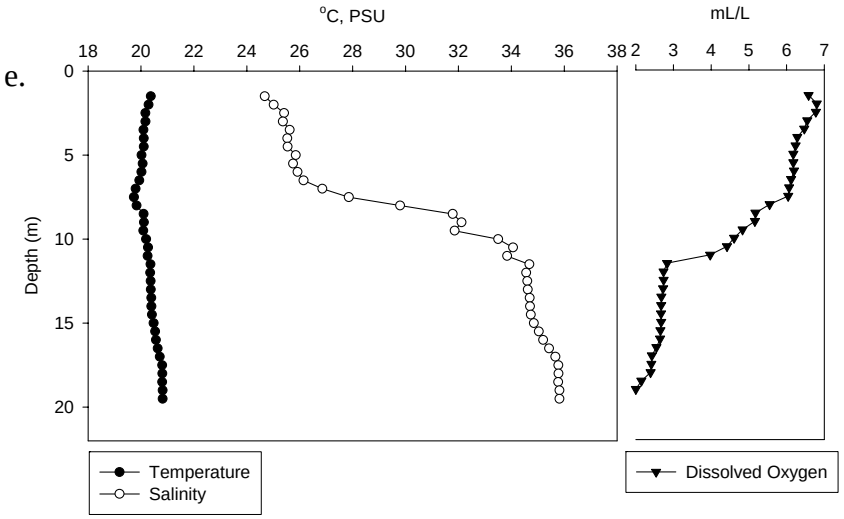


Fig. 18 (Continued).

e.



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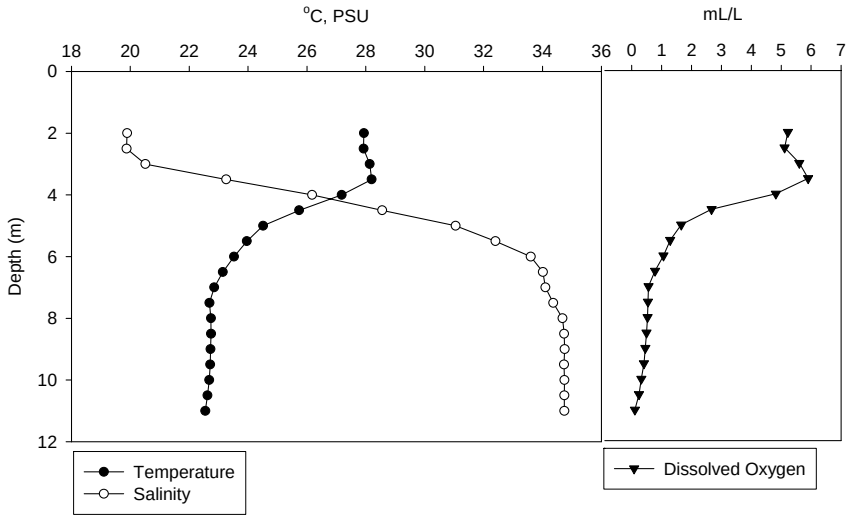

Fig. 18 (Continued).

VITA

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Texas A&M University, Galveston, TX
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Advisor – Dr. Gary A. Gill

Roger Williams University, Bristol, RI
Bachelor of Science (with honors) 5/2003
Majors: Marine Biology, Environmental Chemistry
Minor: Mathematics

Field Experience:

Research Assistant, CALFED Bay-Delta Program
Texas A&M University, Moss Landing Marine Lab
California Delta Region (7/2004, 12/2004, 4/2005, 7/2005)
Water and sediment collection, benthic flux chamber, pore water sampling

Research Assistant, R/V *Gyre* and R/V *Pelican*
Texas A&M University, Louisiana Marine Consortium
Gulf of Mexico (8/2004, 10/2004, 3/2005, 6/2005)
CTD casts, water chemistry, box coring

Presentations:

American Chemical Society National Convention
New Orleans, LA (3/2003) – Poster: Analysis of Contaminant Levels in Various Tissues of Local Seals

Orlando, FL (4/2002) – Poster: Heavy metal phytoremediation and the production of heat shock proteins

NIH/BRIN Convention
West Greenwich, RI (6/2002) – Poster: Physiological response to heavy metal exposure in *Mercenaria mercenaria*

Laboratory Skills:

Maintenance and operation of the following:
GC/CVAFS, Non-dispersive Atomic Fluorescence Spectrometer, Direct Mercury Analyzer, GF and FAAS, Microelectrode

Sample Preparation and Measurement of the following:
MMHg in sediment (EPA Method 245) & water (EPA Method 1631),
Total Hg in sediment (EPA Method 7473) & water (EPA Method 1631)

Ultra Clean technique (EPA Method 1669)
Cleaning, sample collection, and sample preservation