DISSOLVED GASEOUS MERCURY BEHAVIOR IN SHALLOW WATER

ESTUARIES

A Thesis

by

CHARLES MELCHOR LANDIN

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

December 2007

Major Subject: Oceanography

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Approved by:

Chair of Committee,   Peter Santschi
Committee Members,   Robin Autenrieth
                        Robert Duce
Head of Department,   Robert Stickney

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ABSTRACT

Dissolved Gaseous Mercury Behavior in Shallow Water Estuaries. (December 2007)

Charles Melchor Landin, B.S., Texas A&M University at Galveston

Chair of Advisory Committee: Dr. Peter Santschi

The formation of dissolved gaseous mercury (DGM) can be an important pathway for mercury removal from an aquatic environment. DGM evasional fluxes from an aquatic system can account for up to 95% of atmospheric Hg and its deposition pathways. While this makes DGM an important species of mercury to investigate, the difficulty of accurately analyzing DGM has prevented many from studying it. In this study, DGM was measured in two different types of estuarine environments and with two different methods, discrete and continuous analysis. The discrete technique works reasonably well and is reproducible, but it does not allow one to observe rapid changes in DGM concentration due to long analysis times (~2 hr per sample).

When used in this study, the discrete sampling technique agreed well with the continuous technique for Offatts Bayou, Galveston, Texas, and Georgiana Slough in the California Bay-Delta region. The average DGM concentration during the March continuous study at Offatts Bayou was 25.3 ± 8.8 pg L^{-1}. This is significantly higher than the average DGM concentration from Georgiana Slough during late March 2006 (9.6 ± 6.6 pg L^{-1}). DGM seemed to correlate best with photosynthetically active radiation (PAR) data in every study, suggesting that the primary control of its formation is solar irradiation. Stronger positive correlations with PAR were seen when DGM data was

shifted back one hour, indicating that mercury photoreactions take time to complete. DGM also correlated positively with wind speed in most instances. However, increased wind speed should enhance air to water transfer of elemental mercury, thus one would expect a negative correlation. DGM co-varied negatively with salinity during the continuous studies, suggesting that the DGM pool is reduced in surface waters by chloride mediated oxidation.

Three predictive flux models were used in the study to assess the potential for DGM water to air transfer. For both the Georgiana Slough and Offatts Bayou studies, the predicted flux dropped to or below zero after sunset. This study does contribute to the understanding of DGM cycling in aquatic environments as there are few studies that have made continuous DGM measurements in estuarine environments.

DEDICATION

To my parents David and Patricia Landin and to the rest of my family: Doug, Christina,

Lance, Gelsey, Alexis, A.J., and W.L.

- I love you all.

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I would also like to thank Wes Heim, Amy Byington, Mark Stephenson, Kenneth Coale and the other faculty / staff of Moss Landing for their help and efforts with collecting my data in California.

Last but not least, to Peter Santschi, who took the helm as my committee chair when Gary left and whose confidence in me gave me the inspiration and motivation to finish this work. And I would like to thank Robert Duce and Robin Autenrieth for serving on my committee as well.

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1. INTRODUCTION

1.1 General Background

Mercury, an element named after the "Winged Messenger" in Roman mythology, can exist in many chemical and physical forms in natural waters (Hines and Brezonik, 2004). The speciation of mercury ultimately governs its bioavailability, toxicity, and biogeochemical cycles in the aquatic environment (Bloom, 1992; Benoit et al., 2001; Choe et al., 2003; Mason and Fitzgerald, 1993; O'Driscoll et al., 2003a&b). In estuaries and the ocean, total mercury typically exists in picomolar concentrations (Gill and Fitzgerald, 1988). Some of the prevalent forms of mercury in natural waters include: dissolved inorganic mercury species [Hg(II)], dissolved gaseous mercury [Hg^o (aq)], monomethyl mercury (CH_3Hg^+), and particulate adsorbed mercury species. Dissolved inorganic mercury species [Hg(II)] are argued as being the most particle-reactive forms mercury (Han et al., 2006), but mercury adsorbed onto colloids, which are particles 1 nm – 1 μm in diameter, can be particle-reactive, too (Choe et al., 2003; Tang et al., 2002). There is evidence in support of monomethyl mercury (MMHg) being biotically produced by sulfate reducing microbes (Benoit et al., 2001). MMHg is a potent toxin that can cause severe damage to the kidneys and the central nervous system (Clarkson, 1997). MMHg is also known to bioaccumulate in aquatic food chains (Bloom, 1992; Watras and Bloom, 1992). Through bioaccumulation, MMHg can be found in predatory fish at levels 10^6 times greater than in the water column, which can be a significant health risk to populations whose main staple is fish (Watras and Bloom, 1992; Poulain et al., 2004).

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This thesis follows the style of *Geochimica et Cosmochimica Acta.*

Much attention has also been focused toward mercury in the adsorbed particulate phase (Choe et al., 2003), because as particulate matter settles organic matter will oxidize and release mercury in the dissolved form, thus remobilizing the mercury before it can be buried in the sediment sink. It has been demonstrated that the cycling of elemental mercury (Hg^o) is of great importance to Hg transport, residence time, as well as reactivity in natural waters (Amyot et al., 1997b; Mason et al., 1994; Mason and Sheu, 2002; Morel et al., 1998). Dissolved gaseous mercury (DGM) is mainly in the form of elemental mercury in lakes, estuaries, the surface ocean, and rivers (Amyot et al., 1997b). Other volatile mercury species, such as dimethyl mercury, can be present at depth in the ocean (Amyot et al., 1997b).

Redox reactions of mercury play a major role in the cycling of mercury between land, air, water, and sediment (Hines and Brezonik, 2004; Watras et al., 1995). In the atmosphere, mercury exists predominantly as elemental mercury at a concentration of approximately 1.5 ng m^{-3} in the Northern Hemisphere. In the Southern Hemisphere, gaseous elemental mercury (GEM) is approximately 1 ng m^{-3}. The tropospheric residence time for GEM is approximately 1 year (Temme et al., 2003). The oxidized form of mercury in the atmosphere is referred to as reactive gaseous mercury (RGM). It is speculated that Hg(II) in air aloft is the primary form of reactive gaseous mercury (RGM) (Engle et al., 2005; Han et al., 2004; Poissant et al., 2005; Shon et al., 2005; Temme et al., 2003). According to Engle et al. (2005), RGM is formed primarily from photooxidation and ozone mediated oxidation. When gaseous elemental mercury is oxidized to reactive gaseous mercury, it becomes much more water soluble (O'Driscoll et al., 2003). RGM is very particle and water reactive, thus upon contact with precipitation

RGM will become aqueous Hg(II) species. RGM is the intermediate phase between the gaseous elemental and dissolved Hg (II) precipitation and aerosol phases. Hence, Hg(II) is the predominant form of mercury in precipitation (O'Driscoll et al., 2003b; Amyot et al., 1997a). This is an important pathway of mercury entry into an aquatic ecosystem (Mason et al., 1999; 2001; Xu et al., 1999).

Mercury concentrations in any water body are due to a balance between inputs (e.g. deposition and runoff) and outputs (e.g. volatilization and sedimentation). Due to the low solubility and high Henry's Law constant of Hg(0), evasional fluxes account for 7-95% of the estimated atmospheric Hg deposition in a freshwater system (Amyot et al., 1994; O'Driscoll et al., 2003a&b; Rasmussen, 1994; Siciliano et al., 2002). Dimethyl mercury can contribute up to 0.75% of the DGM signal, but little is known if any other species other than elemental mercury contribute to the DGM signal (O'Driscoll et al., 2003a&b). There are many biotic and abiotic pathways that can produce DGM through reduction or oxidize DGM to more labile Hg(II) (Lindberg et al., 2000). Figure 1 shows the competing pathways that mercury may take in an aquatic ecosystem after deposition.
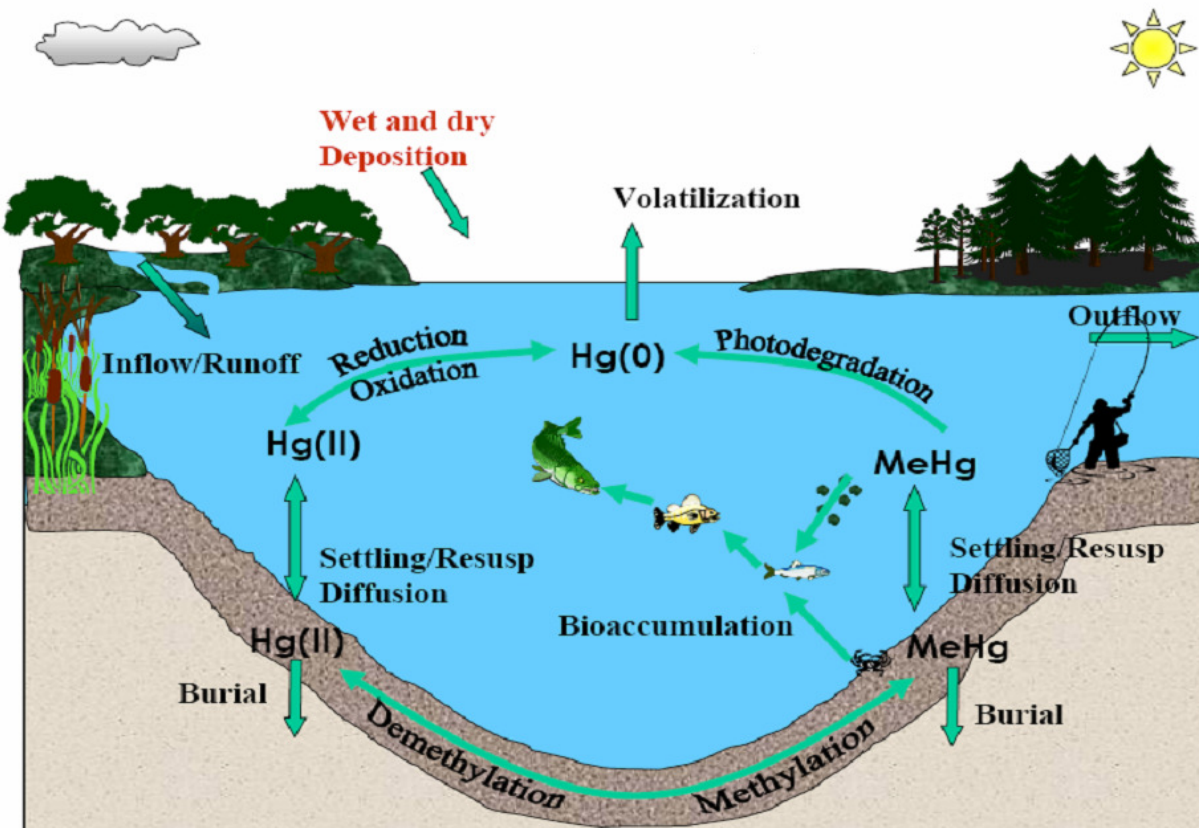
Figure 1: A diagram of the competing pathways of mercury in an aquatic ecosystem.

1.2 What Is Currently Known

      Dissolved gaseous mercury production and consumption has been documented by many authors. In high Arctic lakes, Amyot et al. (1997a) note that mercury has been bioaccumulating in indigenous populations as a result of consuming contaminated fish. And the mercury present in the high Arctic lakes is due in part to long range atmospheric transport of gaseous phase mercury (Amyot et al., 1997a; Poulain et al., 2007). Amyot et al. (1997a) also suggest that the Arctic may be a global sink for mercury and other aerosols. In this study of the high Arctic lakes, there was a significant positive relationship between solar radiation and DGM production caused by photoreduction. In lakes containing medium to high dissolved organic carbon, DGM production may be limited to biotic reductive processes; but in clear waters DGM may be produced photochemically by UV radiation (Amyot et al., 1997a; Amyot et al., 1994).

      The reverse reaction of photoreduction is photooxidation (i.e. Hg(0) $\rightarrow$ Hg(II)) which has been documented by Lalonde et al. (2001). Solar radiation can promote both oxidation and reduction of DGM through direct and indirect pathways (Amyot et al., 1997b; Hines and Brezonik, 2004; Schroeder et al., 1991). The peak absorption by Hg(0) occurs at 253.68 nm, but radiation <290 nm in wavelength does not reach the lower atmosphere in mid to low latitudes, so direct oxidation of Hg(0) in the troposphere is unlikely (Hines and Brezonik, 2004). A phenomenon known as "polar sunrise" can take place at high latitudes, and during this process UV radiation will produce large atmospheric concentrations of reactive gaseous mercury (RGM) from indirect oxidation of Hg(0), which is bioavailable if deposited (Lindberg et al., 2002). At lower latitudes,

less attention has been given to similar reactions producing RGM (Hines and Brezonik, 2004).

UV radiation can also yield other reactive species. These reactive species can be oxygen radical compounds with environmental half-lives less than one second (Hines and Brezonik, 2004). Other studies have shown that Hg^0 (aq) (DGM) can be oxidized by hydroxyl radicals (Gardfeldt et al., 2001), singlet oxygen, and ozone (Hall, 1995; Hines and Brezonik, 2004). Some other oxidants for DGM include organoperoxides and organic compounds (humics). In seawater, DGM can undergo oxidation that is chloride ion mediated (Amyot et al., 1997b). Losses of Hg^0 can also occur in the dark from long lived photo-produced oxidants or non-photoproduced processes (Hines and Brezonik, 2004). In fact, it has been proposed that hydrogen peroxide from sunlight induced transformations of dissolved organic carbon (DOC) can act as a reducing agent for Hg(II) or oxidizing agent for Hg^0 depending on pH (Schroeder et al., 1998; Wigfield and Perkins, 1985). The following two reactions for this process have been proposed (Amyot et al., 1994):

$$H_2O_2 + 2H^+ + Hg^0 \rightarrow 2H_2O + Hg^{2+}$$

$$H_2O_2 + 2OH^- + Hg^{2+} \rightarrow O_2 + 2H_2O + Hg^0$$
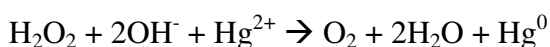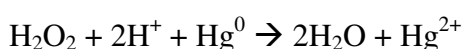
High DOC concentrations have been known to directly affect Hg redox chemistry. DOC tends to complex Hg(II), which affects is availability as a reduction substrate (Allard and Arsenie, 1991). DOC also interferes with light penetration. Chromophoric DOC (CDOC) can absorb light in the UV range and form photoreactive intermediates that can alter the redox state of Hg (Alberts et al., 1974). It has been observed that DGM photoproduction in seawater is quite low compared to temperate freshwater systems.

However, if it is normalized to total Hg in the water, then photoproduction is quite faster in seawater than in freshwater. This result is likely due to the low DOC content in seawater systems; only a small fraction of Hg is complexed while the majority is easily reducible (Lanzillotta and Ferrara, 2001; Lanzillotta et al., 2002).

Another important source of DGM production is elimination of ionic mercury through biota (via reduction) (Siciliano et al., 2002; Mason et al., 1995), and heat catalyzed reduction of Hg(II) to Hg(0) (Allard and Arsenie, 1991). Some of the biological mechanisms by which Hg(II) is reduced to Hg (0) are understood, but not much work on the role of biotic activity in diel DGM patterns has been done (Siciliano et al., 2002; Smith et al., 1998). It has been shown that DGM is correlated with certain phytoplankton pigments, but that may be due to nonspecific reactions as a result of microbial growth (Siciliano et al., 2002). In freshwaters, however, heterotrophic bacteria may play a role in DGM production (Siciliano et al., 2002).

Microbial activity can indirectly influence DGM levels. For instance, bacterial enzymes induced by H_2O_2, e.g. hydroperoxidase-catalase (KatG), oxidize Hg^0 to more particle-reactive Hg(II) (Siciliano et al., 2002; Smith et al., 1998). H_2O_2 follows a strong diel pattern with increasing levels of H_2O_2. So, H_2O_2 does not directly oxidize Hg^0 in this case, but induces the release of KatG and other enzymes because the bacteria need to protect themselves from hydrogen peroxide's harmful effects on an intracellular level (Siciliano et al., 2002; Smith et al., 1998). This is analogous to mercury methylation resulting from sulfate reducing bacteria being stimulated by the presence of increased sulfate (Mason et al., 1999). As labile mercury (mostly Hg(II)) is methylated, the amount of photoreducible Hg declines, thus reducing DGM production (Rolfhus and Fitzgerald,

2004). Amyot et al (1997b) suggest that Hg(II) may limit DGM production as it is a photoreducible and a methylation substrate.

Mercury is also known to behave nonconservatively in estuaries (Benoit et al., 1998; Choe et al., 2003; Costa and Liss, 1999; Mason et al., 1993). In highly productive estuarine waters, Hg can undergo reduction and oxidation reactions through various pathways. Reduction of Hg via metabolic processes of photosynthetic and non-photosynthetic prokaryotes and eukaryotes can be a significant source of DGM production in estuaries (Mason et al., 1999). Biotic reduction can account for as much as 40% of the total DGM production (Amyot et al., 1997b). In addition to biotic reduction and photoreduction, Hg (I) and Hg (II) can be reduced in the presence of humic or fulvic acids (Costa and Liss, 1999). Another feature of estuaries that can influence the biogeochemistry of Hg is the presence of macrophytes, which are aquatic plants that are accustomed to water-saturated soils. Macrophytes can release reducing/oxidizing compounds or nutrients, which can enhance microbial activity (Garcia et al., 2006). Also, root uptake of Hg and its translocation to above ground tissues may be a path for remobilization of Hg buried in sediments (Coquery and Welbourn, 1994; Garcia et al., 2006).

In seawater, it has been proven that DGM can be readily oxidized via chloride ion mediation (Amyot et al., 1997b; Costa and Liss, 1999; Yamamoto, 1996). Oxidation may be as important as volatilization in the depletion of the Hg^0 pool in seawater (Amyot et al., 1997b; Costa and Liss, 1999; Mason et al., 1999). The Hg oxidation mechanism involving chloride mediation is not well known. The chloride ion may stabilize oxidation products and thus promote the oxidation reaction (Amyot et al., 1997b).

While there have been several studies on dissolved gaseous mercury behavior in natural waters, there have been very few studies that examine the relative importance of light and dark reactions or temporal trends of DGM in estuaries (Rolfhus and Fitzgerald, 2001; 2004). Also, DGM concentrations have been known to change by as much as 50 % within a 20 minute period (O'Driscoll et al., 2003a;b).

For this study, DGM dynamics were assessed in two regions: the Galveston Bay region and the San Francisco Bay-Delta region. The temporal trends of DGM concentrations were observed in this study as well.

1.3 Hypothesis and Scope of the Study

The available information of the cycling of DGM in estuaries is sparse. Based on information obtained in freshwater systems, one can hypothesize that processes affecting DGM cycling are similar in estuarine systems. The hypothesis that was tested in this research is as follows:

> Dissolved gaseous mercury concentrations and distributions in estuaries are highly dynamic, exhibiting rapid concentration changes and temporal and spatial trends that are influenced by several environmental parameters such as sunlight intensity, dissolved oxygen, salinity, and temperature.

To test this hypothesis, a series of laboratory and field experiments were performed. The work conducted is outlined below. The main effort of this thesis was to determine temporal trends of DGM concentrations in Galveston Bay and the San Francisco Bay-Delta sampling sites. Specific details include:

- Sampling of DGM in the San Francisco Bay-Delta region was conducted during six field trips between 2004 and 2006 (Table 1). The two principal sites were Little Break and Mandeville Bay. Several other sites were sampled as well.

- Similarly, profile sampling in Offatts Bayou consisted of approximately one trip every one to two months between January 2006 and August 2006.

- Surface water samples were collected for discrete and continuous modes of DGM analysis (described below) for both estuarine sites. Results from the continuous and discrete methods were compared.

- In Offatts Bayou, samples were collected between 0-10 m depth for approximately five depths, and analyzed in discrete mode to observe spatial trends of DGM

concentrations. The DGM concentrations may be controlled by processes other than sunlight as depth increases. The DGM depth profile could have a temporal trend, as well.

- The continuous system was set up at Offatts Bayou in Galveston, TX and at Georgiana Slough in Oakley California. The system ran continuously for several 24 hour periods during the spring and summer months for the purpose of observing temporal DGM trends. These surface water trends were compared between the Texas and California sites.

- The water to air DGM flux in the San Francisco Bay-Delta and Galveston Bay was calculated using different approaches, and the advantages and disadvantages of each method will be assessed.

- The light intensity, dissolved oxygen, water temperature, and salinity were measured at the time of DGM data collection for both continuous and discrete modes.

1.4 Objectives

1. Develop an automated system that can effectively increase temporal resolution of measuring DGM samples to approximately 3 per hour.

2. Assess spatial and temporal variation in estuarine DGM concentrations.

3. Determine the relationship between DGM concentrations and environmental parameters (salinity, dissolved oxygen, water temperature).

2. SITE DESCRIPTION

2.1 San Francisco Bay-Delta

Mercury in the San Francisco Bay-Delta region has long been a concern. Water column concentrations of mercury often exceed the California state standard of 12 ng L^{-1}, and there have been advisories on the consumption of certain species of fish due to Hg contamination (Domagalski, 1998; 2001). During the Gold Rush in the Sierra Nevadas, large amounts of Hg were used to extract gold. Now this Hg is running off into the Sacramento and San Joaquin Rivers and is contaminating San Francisco Bay.

San Francisco Bay is one of the largest estuaries on the Pacific coast; it has an average depth of 6 m and a surface area of 1,240 km^2. San Francisco Bay has two fresh water sources: the Sacramento River and the San Joaquin River. This study encompassed various sites in the northern reach, which is defined as the upper estuary containing Mandeville Bay, Suisan Bay, Honker Bay, Little Break, and Georgiana Slough. The Sacramento River drains ~80% of the freshwater entering San Francisco Bay (California Data Exchange Center, http://cdec.water.ca.gov). The sampling sites in the northern reach have very low salinity (S<1.0) and are surrounded by much vegetation such as reeds and water hyacinth. A map of the San Francisco Bay-Delta with sampling sites can be seen in Figure 2. All of the coordinates for the sites are in Table 1.

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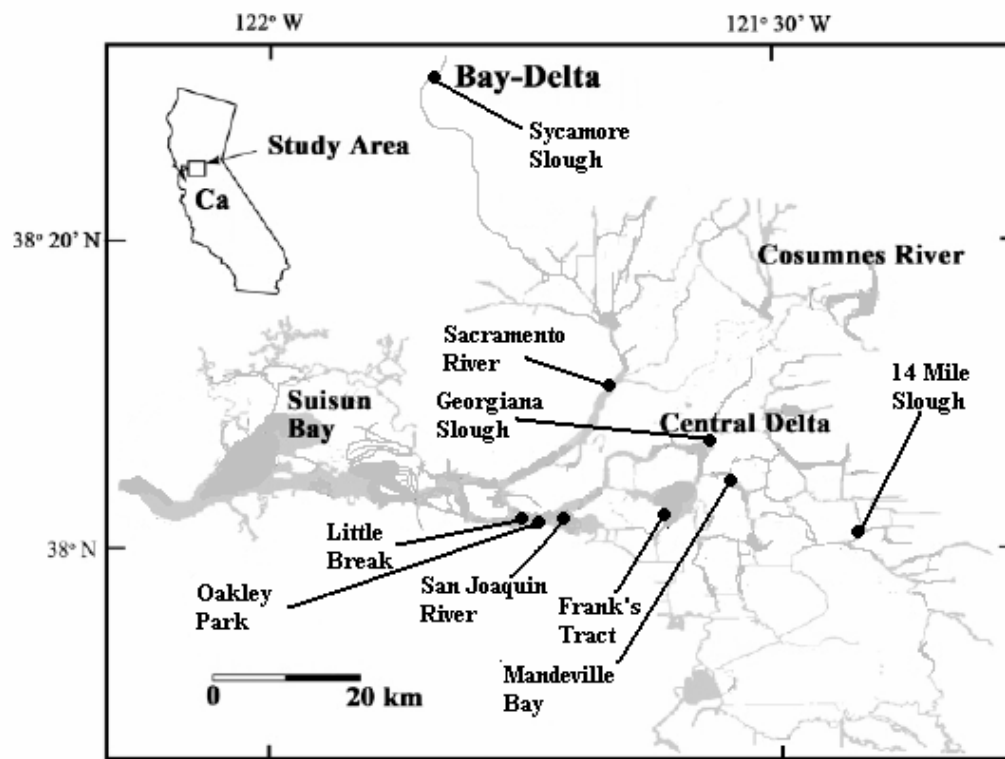
Figure 2: The San Francisco Bay-Delta.

Table 1:Discrete sampling sites in the California Bay-Delta with coordinates and times of sample collection.

Site	Latitude	Longitude	Time(s) Sampled (PST)
14 Mile Slough	38°00'18" N	121°23'45" W	07/20/2004 13:00
Cosumnes River	38°16'16" N	121°23'22" W	07/18/2004 12:00
Georgiana Slough	38°07'48" N	121°34'46" W	12/12/2004 15:00
			12/12/2004 17:00
			03/16/2005 10:15
Frank's Tract	38°03'00" N	121°36'06" W	07/18/2004 12:00
Little Break	38°01'41" N	121°45'40" W	10/17/2005 13:51
			03/17/2005 15:15
			07/12/2005 09:50
Mandeville Bay	38°04'00" N	121°32'03" W	07/19/2004 12:00
			12/13/2004 13:35
			12/14/2004 15:00
			03/15/2005 12:30
			03/16/2005 16:30
			07/14/2005 18:00
			10/18/2005 09:30
			10/19/2005 14:45
Oakley Park	38°01'15" N	121°45'02" W	07/12/2005 12:15
			07/13/2005 14:30
			10/18/2005 14:56
			10/18/2005 20:35
			10/20/2005 09:22
Suisun Bay	38°03'32" N	121°56'30" W	07/20/2004 13:00
Sycamore Slough	38°42'51" N	121°42'40" W	12/12/2004 17:00

2.2 Galveston Bay Region

Galveston Bay (map seen below in Figure 3) is a shallow water estuary with an average water depth of ~2 m and a low tidal range (<0.5 m). It is also a well-mixed estuary with an average salinity of 30. The average water temperature in the summer is $28^{o}C$, whereas it is $10^{o}C$ in the winter. Galveston Bay is surrounded by heavy industrial complexes and supports 50% of the total chemical production in the United States and 30% of the U.S. Petroleum industry (Ditton et al., 1989). Many trace metals such as Hg, Cu, Zn, and Pb behave non-conservatively in Galveston Bay (Wen et al., 1999) and have industrial anthropogenic sources as well.

Offatts Bayou is a major part of the Galveston Bay estuary system and is surrounded on the sides by the city of Galveston, Texas. During the beginning of the 20th century, the city of Galveston used this marshy inlet as a borrow pit for major construction projects, resulting in the creation of an artificial basin with an area approximately 1 km x 2 km, and a maximum depth of 11 m, which is approximately 2 to 5 times deeper than the surrounding waters. A narrow channel that is approximately 3 m to 4 m deep is the primary avenue of a restricted exchange of waters with the adjacent West Bay (Fig. 3) (Cooper and Morse, 1996).

The deeper waters of Offatts Bayou are sulfidic (Cooper and Morse, 1996; Han et al., 2006; and based on smell) from late spring to early winter. The deeper waters become extremely depleted in oxygen when there is high sulfide content. It has been shown that these geochemical conditions can have a significant effect on mercury speciation (Benoit et al., 2001). Thus, this basin is an intriguing site that will continue challenge studies of the geochemical cycling of Hg.
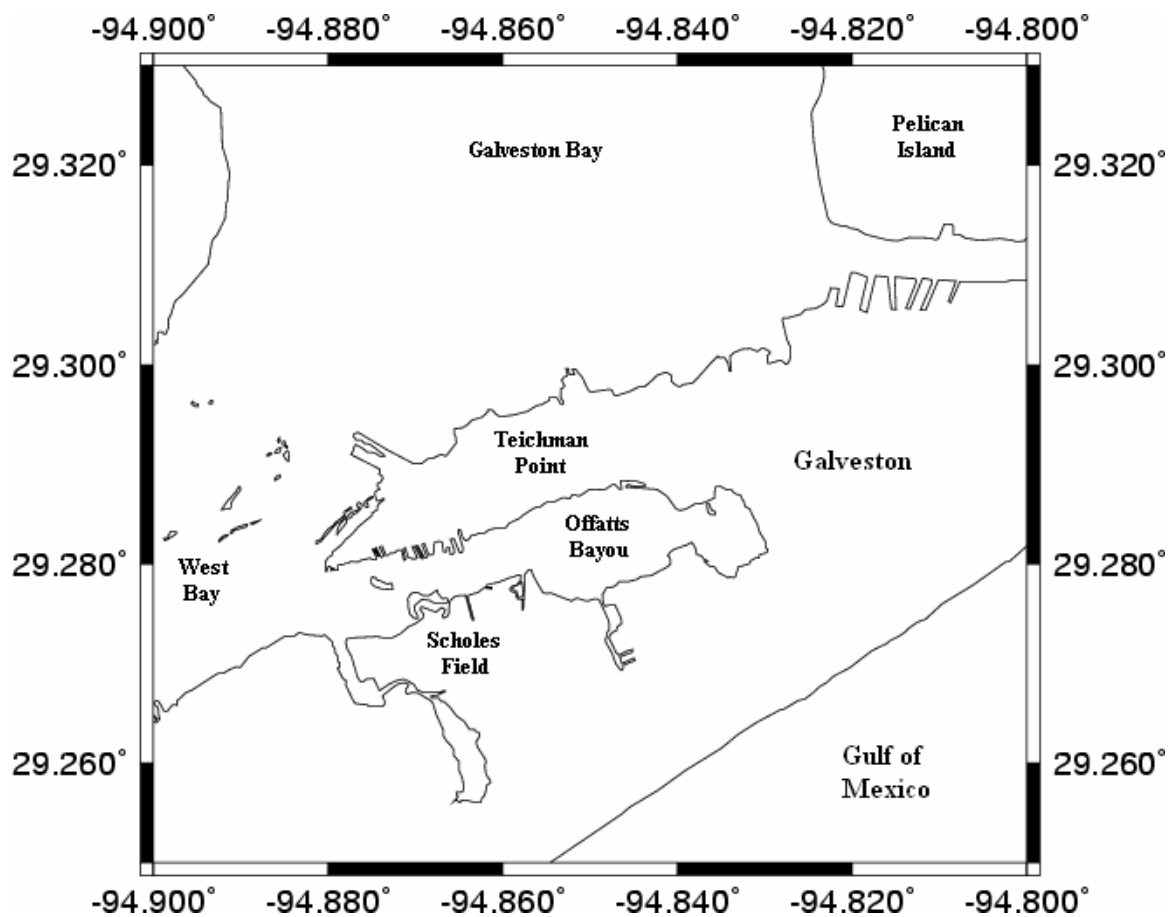
Figure 3: Map of Offatts Bayou and surrounding region. The continuous measurements were performed at 29°17.1' N, 94°50.4' W.

2.3 Site Differences

One difference between Galveston Bay and the SF Bay-Delta is that they both have different sources of anthropogenic mercury. The SF Bay-Delta region receives a significant source of mercury via rivers from historic mining practices. Another difference is the depth of the diagenetic transition from O_2 reduction to SO_4^{2-} reduction. In the SF Bay-Delta, the transition is at or below the sediment – water interface. In Offatts Bayou (Galveston Bay), the transition is within the water column between 0 to 10 m depth during summer and fall (Cooper and Morse, 1996). Photoreducible mercury can be methylated below the O_2 boundary, thus reducing DGM production (Rolfhus et al., 2004). Moreover, Offatts Bayou is substantially more saline ($S \approx 30$) than the SF Bay-Delta ($S<1.0$). In Galveston Bay, there should be diminished DGM production due to chloride mediated oxidation, as DGM oxidation via chloride has been documented in several studies (Amyot et al., 1997b; Rolfhus and Fitzgerald, 2001; 2004; Tseng et al., 2003; Yamamoto 1996).

3. METHODOLOGY

3.1 Background

DGM is present in pristine systems at fmol L^{-1}, while total mercury is in concentrations of pmol L^{-1}. Therefore, it is a challenge to measure DGM accurately (O'Driscoll et al., 2003b; Tseng et al., 2003). Most investigators to date have used a "two stage gold amalgamation approach" in which a water sample is purged with inert gas and mercury collected on gold sand traps (O'Driscoll et al., 2003a&b; Lindberg et al., 2000); after which the Hg^0 on a Au sand trap is desorbed in an analytical gas train (Fitzgerald and Gill, 1979). This technique is accurate and reproducible, but has several limitations. The time for purge and analysis can range from 20 to 90 minutes. Furthermore, this system involves the manual handling of samples and analytical steps that are not integrated (i.e. separate purge and analytical steps). In the two stage approach, there are risks of sample contamination and leaks in the purge system. Another limitation is that there are no "long-term" sample preservation methods for DGM (Lindberg et al., 2000; O'Driscoll et al., 2003a&b; Tseng et al., 2003), and DGM loss rates from samples in sealed containers with no headspace can range from 10 to 20% h^{-1}. This is likely due to oxidation (O'Driscoll et al., 2003a&b). Another concern is blank control from the storage time of the Au sand columns before analysis (Tseng et al., 2003).

It has been reported that DGM concentrations can change in surface water by 50% within 20-30 minutes (O'Driscoll et al., 2003b; Siciliano et al., 2002; Tseng et al., 2003). In order to see realistic changes in DGM, a portable and reliable system that can measure fM concentrations in a short period of time with good reproducibility is needed. There has been little work on the development of such a system (O'Driscoll et al., 2003

a&b; Tseng et al., 2003). This created the impetus for me to develop a continuous analysis system that has integrated the purging and analytical capabilities in order to observe higher resolution DGM data that are not available in discrete collection/analysis methods.

3.2 Sample Collection/Discrete Mode

Sampling was conducted in the San Francisco Bay-Delta region during six field trips from 2004-2006. Samples of surface water were collected from ~3 different sites per trip for the determination of DGM. Duplicate samples were collected at each site near the water surface (~15 cm depth) in acid cleaned 2-L Teflon bottles. The samples were kept cold (~4°C) and in the dark until time of purging. The time of day the samples were collected, light intensity, and YSI® data (temperature, salinity, and D.O.) were noted. At times, samples were collected three times per day (morning, noon, night) and the temperature, salinity, and D.O were noted to observe potential diurnal patterns.

In Offatts Bayou (Galveston Bay), near surface water samples were collected as well as water samples with depth (up to 10 meters) to observe the DGM trend with decreasing sunlight and decreasing oxygen. Dissolved oxygen decreases rapidly with depth in Offatts Bayou (Galveston Bay). Sampling frequency was around one trip every one to two months from January 2006 – August 2006, and 5 samples between 0 m and 10 m depth were collected. A duplicate sample for at least two depths was also collected. Also, sampling times for all trips were conducted in late morning (9:30 – 11:30 CST), when DGM production is anticipated to be highest. The water samples were pumped through acid cleaned Teflon tubing into acid cleaned 2-L Teflon bottles and filled until no head space was remaining. The bottles were kept cool and in the dark until purged. The

caps on these bottles form a reliable seal so sample loss from degassing should be minimal (Tseng et al., 2003; Amyot et al., 1997b). In fact, DGM loss in sample bottles is caused primarily from oxidation that may be photo-induced or chloride ion mediated (Amyot et al., 1997b). In some cases, oxidative loss may be caused by biological production. When samples are kept cool and dark, the storage time can be from 4-6 hours with no significant oxidation/production of DGM within the bottle (Poulain et al., 2004; Tseng et al., 2003).

3.3 Measurement of DGM in Discrete Samples

Initially, samples were carefully poured (to minimize DGM loss) into a 2-L Teflon sparger that contains a glass frit approximately 1 cm from the bottom of the sparger. There was little head space between the sample water and the top of the sparger. The sparger was closed air tight to avoid sample loss. Samples were purged with ultra-high purity nitrogen gas that was further purified of Hg with a gold trap. The purge time is dependent on the volume of the sample and the flow rate of the carrier gas (Lindberg et al., 2000). The sample volume in discrete mode is approximately 2-L. During purging, the N_2 carrier gas transports the sample first through a soda lime trap to remove water vapor. Then, the sample is amalgamated onto a gold trap that is subsequently sealed in a test tube and transported to the lab. Purge blanks were also collected.

Later, the Teflon sparger was replaced with a 2-L Teflon bottle fitted with a Savillex® two-fitting cap (figure 4). The Teflon bottle apparatus provided a more reliable seal than the sparger apparatus. One fitting allowed the purge gas to enter the bubbler through a Teflon tube with a glass frit on the end that was suspended ~1 cm from the bottom of the 2-L bottle; while the other fitting allowed transport of the carrier gas and sample through the soda lime trap as described above.

Samples collected onto gold coated sand were analyzed using a two-stage gold amalgamation gas train (Fitzgerald and Gill, 1979). The sample was analyzed using cold vapor atomic fluorescence spectroscopy (CVAFS). Quantification of signals was accomplished using Elab® chromatography software and National Instruments® Labview software. The carrier gas was ultra-pure argon. The gold columns used for sample collection are tested for percent recovery before going into the field and after analysis. Also, the gold columns are blanked before sample collection. A diagram describing this two stage process can be seen below (figure 4).
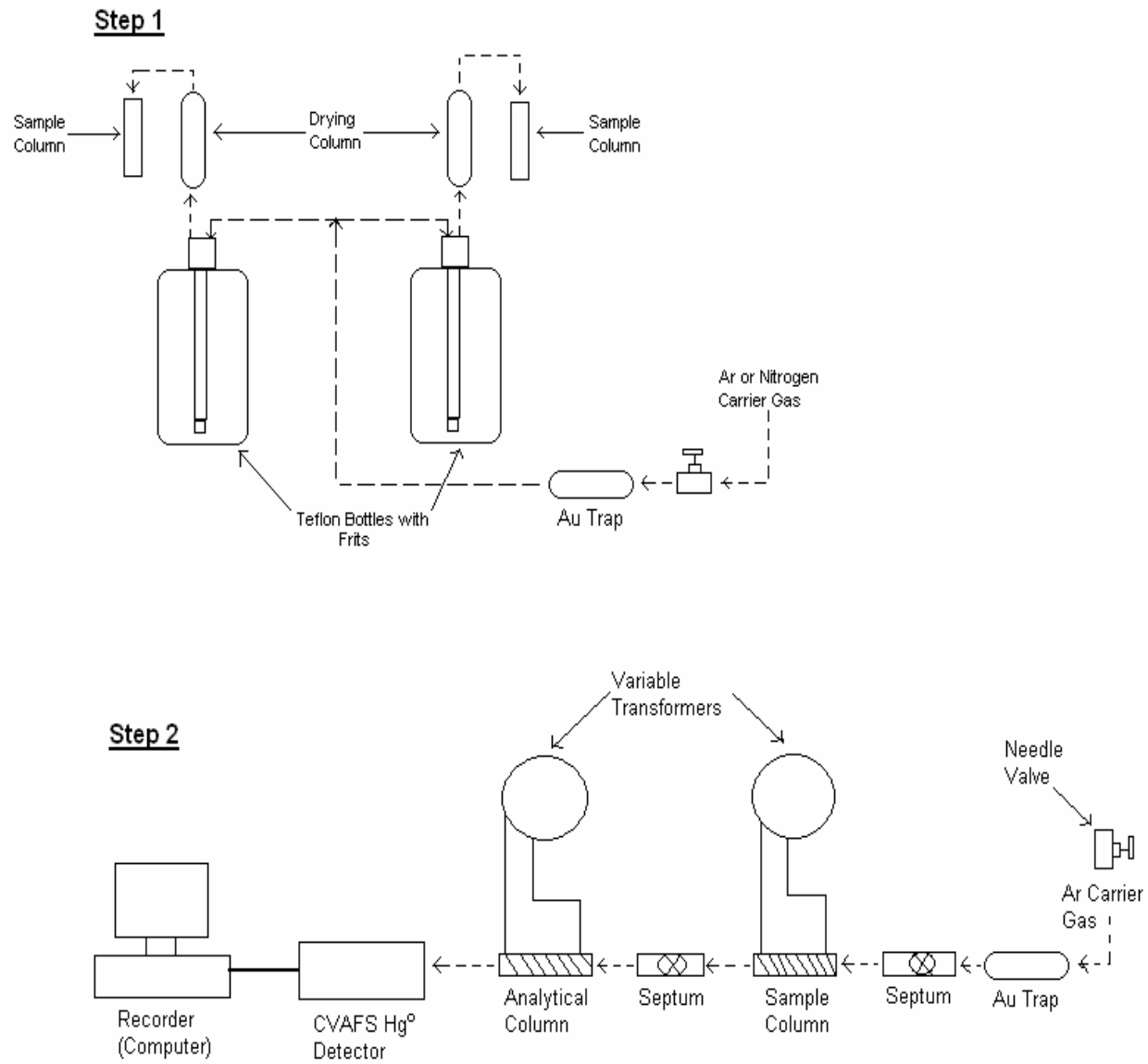
Figure 4: A diagram of the two step discrete DGM analysis system. Step 1 is purging the sample of DGM onto gold sand traps. Step 2 involves thermal desorption of Hg^o from the gold sand traps and then analysis by CVAFS.

3.4 Onsite and Continuous Measurements of DGM

Samples were collected in continuous mode using approaches similar to those described in O'Driscoll et al. (2003b) and Tseng et al. (2003). A YSI® probe was used to continuously collect dissolved oxygen, salinity, and temperature data during sample collection. The continuous analysis system was operated and signals recorded using LabView and National Instruments® components. When operating in continuous mode, a peristaltic pump was used to fill a 2-L glass sparger with water exiting at the bottom. The sample water pump rate was around 1 L min^{-1} and the purge gas flow rate was around 400 mL min^{-1}. The purge time for a 2-L sample in this case would be approximately 25 minutes. The analysis time for the purged Hg^0 is approximately 3 minutes. The sparger was refilled with a new sample every ~30 minutes. A tank of ultra-pure argon gas was used for both the purge and analysis modes. The Ar purge gas enters the sparging vessel through a glass frit near the bottom of the sparger. The DGM is carried with the argon through a soda lime drying column to a gold sand trap where it amalgamates. Periodically, the valve switches the Ar flow to the mass flow controller where the flow is kept at ~60 mL min^{-1}. The Au trap is thermally desorbed by a heating coil and the Hg^0 collected is swept into an atomic fluorescence instrument (Brooks Rand®) and the signal is recorded. The pumps, thermal desorption system, cooling fans, solenoid valves, and CVAFS were controlled by the Labview software using National Instruments® components. Figure 5 seen below summarizes the system used for the continuous analysis of DGM.
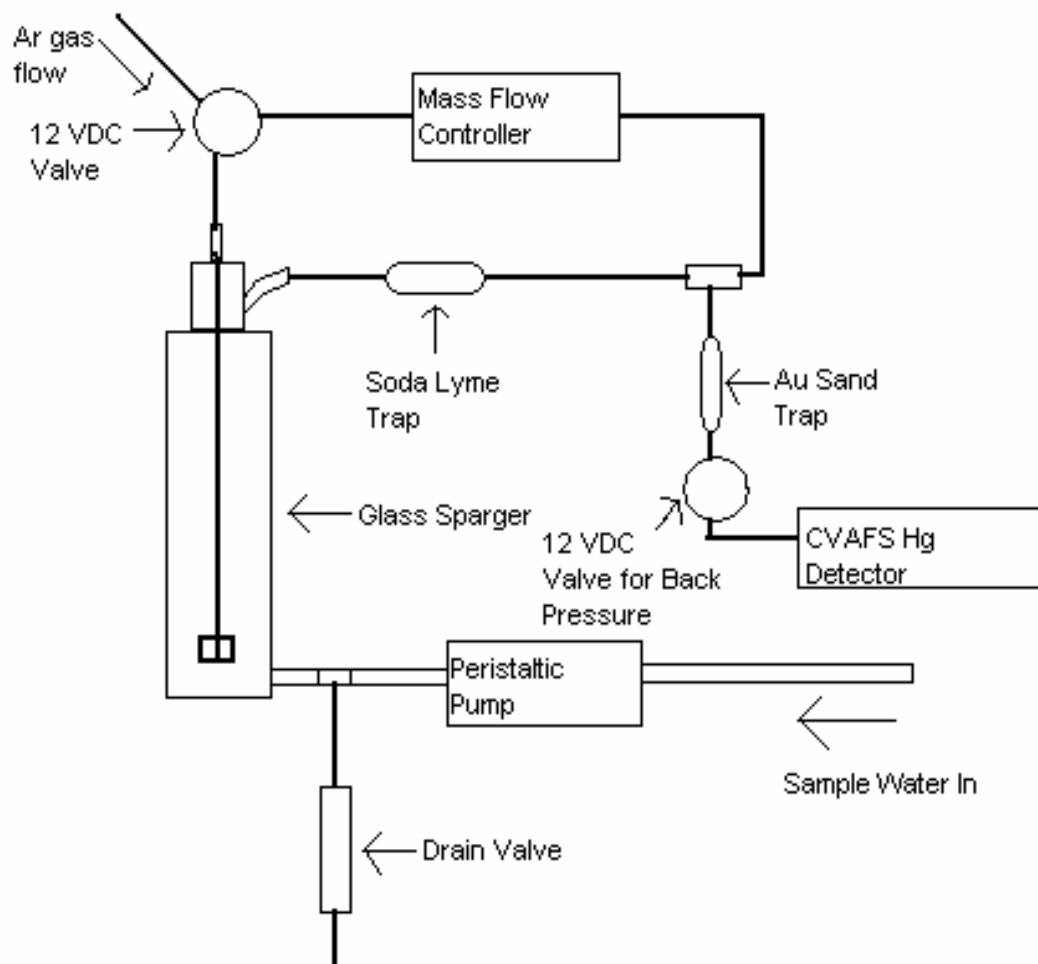
Figure 5: Continuous analysis DGM system

3.5 Calibration

Both the discrete and continuous systems were calibrated using an air standard saturated with elemental mercury. The standard was made by placing a drop of liquid elemental mercury inside a gastight vessel. The standard was allowed to come to equilibrium after 24 hours. In the lab, the standard was then kept at a constant temperature with a constant temperature bath. In the field, a modified Styrofoam cooler with ice water was used. The concentration of Hg^o (g) in the standard is proportional to the temperature as given by Table number 6 in the Tekran® Model-2537A mercury vapor analyzer manual.

The calibration curve was made by plotting the measured peak area of four different Hg^o injection volumes. During continuous analysis a calibration curve was made at times when a big change in DGM concentration was anticipated (e.g. at sunrise and sunset).

3.6 Wind and Sunlight Measurements

Wind measurements for the continuous studies came from local weather stations. For the Offatts Bayou study, wind data was obtained from the Scholes Airfield weather station (EPA site 48-167-0014) with coordinates 29° 15.8' North, 94° 51.4' West. My sampling coordinates in Offatts Bayou were 29° 17.1' North, 94° 50.4' West. So the weather station is approximately 2 km from the Offatts Bayou sampling site. The wind data at the station is reported in m s^{-1} and is averaged every hour. The wind is measured with an anemometer that is 10 m above sea level.

At the Georgiana Slough site (38° 7.8'N, 121° 34.8'W), wind data were obtained from the California Irrigation Management Information System (CIMIS) weather station at Twitchell Island (site 140; 38° 7.0'N, 121° 39.3'W). The wind data are measured at a height of 6.4 m above sea level. The wind data were corrected 10 m using the formula given below from Pond and Pickard (1983).

Sunlight measurements were made with an Apogee Instruments® nanologger that used sensors for UV light and photosynthetically active radiation (PAR). The units were given in μmol photons m^{-2} s^{-1}. When this instrument was not available, solar radiation data (kW m^{-2}) from the weather stations were used.

4. CALCULATIONS

Equation 1: The saturation index (SI) for DGM is calculated as follows from Poissant et al. (2000):

$$SI = \frac{C_{water} \times H'}{C_{air}} \times 100\%$$

where C_{water} and C_{air} are the concentrations of Hg^0 in water and air (ng m^{-3}), respectively, and H' is the dimensionless Henry's Law coefficient corrected for temperature. A value of 1.5 ng m^{-3} will be used for the concentration of Hg^o in the air.

The water to air flux of DGM is calculated according to the following models:

4.1 Mass Transfer Mercury Flux Model (Schroeder et al. 1992)

Equation 2: $F = K_{ol}(C_{water} - C_{air}/H')$

where F is the flux of Hg^0 from water to air (ng m^{-2} h^{-1}), C_{water} and C_{air} are the concentrations of Hg^0 in water and air (ng m^{-3}), respectively, H' is the dimensionless Henry's Law coefficient corrected for temperature, and K_{ol} is the overall mass transfer coefficient in m h^{-1}. K_{ol} can be calculated from

Equation 3: $1/K_{ol} = 1/(H' * K_{air}) + 1/K_{water}$

where K_{air} and K_{water} are respectively the mass transfer coefficients for air and water in m h^{-1}. This model was adapted by Schroeder et al. (1992) from the two-layer gas transfer model of Liss and Slater (1974). The temperature correction for Henry's Law coefficient was made using the relationship from Sanemasa (1975):

Equation 4: $H' = 0.0074(T) + 0.1551$

where T is the temperature (^{o}C) at the water surface (near the air-water interface). In this model, K_{water} and K_{air} are given constant values of 0.09 and 9 m h^{-1}, respectively, and are calculated as follows:

Equation 5: $K_{air}(Hg^0) = K_{air}(H_2O) \times (M_{H2O}/M_{Hg})^{0.5} = 30 \times 0.30 = $ **9 m h^{-1}**

Equation 6: $K_{water}(Hg^0) = K_{water}(CO_2) \times (M_{CO2}/M_{Hg})^{0.5} = 0.20 \times 0.47 = $ **0.09 m h^{-1}**

where M is the molecular mass (g mol^{-1}) of the subscripted compound. However, most

of the resistance to mass transfer for DGM is in the water phase(>99%), hence $K_{water} \approx K_{ol}$

and the air mass transfer coefficient is negligible (i.e. $1/K_{air} = 0.11$) (Schroeder et al.

1992). For this and other models, the average concentration of atmospheric Hg^0 in the

Northern Hemisphere (1.5 ng m^{-3}) will be used.

4.2 Temperature and Wind Sensitive Mass Transfer Mercury Flux Model (Poissant et al.

2000)

Equation 7: $F = K_{ol}(C_{water} - C_{air}/H')$

Equation 8: $K_{water} \sim (0.45U_{10}^{1.64})[Sc_{water}(Hg^0)/Sc_{water}(CO_2)]^{-0.5}$

The Poissant et al. (2000) model was adapted from the two-layer model of Liss and Slater

(1974) and the model of Wanninkhof et al. (1985). This model uses the same formula as

Schroeder et al. (1992) to calculate the flux of Hg^0 in ng m^{-2} h^{-1}. However, K_{water} is

dependent on wind speed at 10 m (U_{10}) and the Schmidt numbers (Sc_{water}) for Hg^0 and

CO_2. Also, K_{water} is in units of cm h^{-1} for the above calculation and converted to m h^{-1} for

the flux calculation. U_{10} can be extrapolated from wind speed measured at any height

with the following expression (Pond and Pickard 1983):

Equation 9: $U_{10} = \dfrac{(U_z)(10.4)}{\ln(z) + 8.1}$

where U_{10} is in m s^{-1} and U_z (m s^{-1}) is the wind speed at a height z (m) above sea level.

The Schmidt number for mercury is calculated by dividing the kinematic viscosity of

water (υ, cm^2 s^{-1}) by the diffusivity of Hg^0 in water (D, cm^2 s^{-1}):

Equation 10: $Sc_{water}(Hg^0) = \upsilon/D$

where υ and D are temperature (T, ^oC) dependent and can be estimated as follows:

Equation 11: $\upsilon = 0.017\exp(-0.025T)$ (Thibodeaux 1996)

Equation 12: $D = (6.0 \times 10^{-7})T + 10^{-5}$ (Kim and Fitzgerald 1986)

The Schmidt number for CO_2 is also temperature (T, ^oC) dependent and can be estimated as follows (Hornbuckle et al. 1994, Bidleman and McConnell 1995):

Equation 13: $Sc_{water}(CO_2) = 0.11T^2 - 6.16T + 644.7$

4.3 Solar Radiation and Wind Speed (Empirically-Derived) Mercury Flux Model (Boudala et al., 2000)

Equation 14: $F = 2.44Rw_s^{1.5} + 1.1$

This is a predictive DGM flux model that is based on near surface wind speed (w_s, m s^{-1}), and solar radiation (R, kW m^{-2}) data taken at Big Dam West Lake in Nova Scotia. A multiple linear regression approach was used to produce this model, which calculates the anticipated mercury flux (F, ng m^{-2} h^{-1}) for a given near surface wind speed and solar radiation. However, many water systems will show different relationships between DGM concentration and solar radiation (Amyot et al., 1997c; Boudala et al., 2000; Hines and Brezonik, 2004). This clearly suggests that the response of DGM concentrations to solar radiation may be controlled by other parameters, such as latitude and DOC concentrations.

5. RESULTS AND DISCUSSION

5.1 Discrete DGM Measurements in California

The mean DGM concentrations obtained with discrete techniques at each site are given in Table 2. Table 3 shows the mean DGM concentrations (from replicate samples) for each time collected at each site. Table 2 also shows mean DGM concentrations taken from other references. The numbers obtained from the Bay-Delta agree reasonably well with published values from other sites. The samples were collected as part of the Calfed Mercury Project (see http://www.delta.dfg.ca.gov/erp/wq_mercuryissues.asp) between July 2004 – April 2006. The samples at all sites were collected from late morning (10:00 PST) to late afternoon (16:00 PST), when DGM production was expected to be highest. One site (Oakley Park) was sampled at three times (morning, afternoon, and night) in an attempt to observe any apparent DGM diurnal variations. The DGM concentrations were blank corrected.

Two blanks were taken after each purge to ensure >95% recovery. The average variance between the first and second blanks for each sample was 0.9 ± 0.5 pg L^{-1}. Since the difference between the first and second blanks was low, only the first blank with each sample was used. This was taken to be the background in the analytical system.

RSD is the relative standard deviation, i.e. the ratio of the standard deviation to the mean. N is the total number of samples at each site. Duplicate samples were collected at the same time to check reproducibility. Sites with only N = 2 samples were sampled at only one time with duplicates being collected for reproducibility. RSD's were somewhat high here, indicating a high variability between samples. The average blank concentration was 5.9 ± 1.5 pg L^{-1}, making the method detection limit 4.6 pg L^{-1} (3 x SD of the blank). Frank's Tract had the highest average measured DGM concentration (40.6 $\pm$ 8.9 pg L^{-1}), but only two replicate samples were collected on July 18, 2004.

Table 2: Discrete DGM data collected from the Bay-Delta during July 2004 - April 2006. The mean, standard deviation, and relative standard deviation for each site is given. N/2 represents the number of times a site was sampled. N is the total number of samples including replicates.

Site	Mean DGM (pg L^{-1})	Standard Deviation	%RSD	N	N/2
Mandeville Bay	6.6	2.9	43.3%	16	8
Oakley Park	15.2	11.0	72.3%	16	8
Little Break	18.3	6.9	37.7%	8	4
Cosumnes River	24.3	7.2	29.8%	2	1
Frank's Tract	40.6	8.9	22.0%	2	1
14 Mile Slough	7.7	3.5	45.6%	2	1
Suisun Bay	4.7	2.2	48.0%	2	1
Sycamore Slough	1.5	0.6	36.6%	2	1
Georgiana Slough	12.9	6.9	53.2%	2	1
1st Blank	5.9	1.6	26.4%	25	
2nd Blank	5.0	1.0	20.0 %	14	
Variance between 1st and 2nd blank	1.0	0.5	54.2%	61	
Total Delta	**14.6**	**12.0**	**82.5 %**	**52**	

Other Studies	DGM (pg L^{-1})	Site
Siciliano et al., 2002	16 - 200	
Krabbenoft et al. 1998	5 – 39	Florida Everglades
Amyot et al., 1994	40 – 120	
Zhang and Lindberg, 2001	29 ± 2	Whitefish Bay, MI

Table 3: DGM concentrations from all discrete sample collection times in the California Bay-Delta. The concentrations given are the average of the replicate samples taken.

Site	Mean DGM (pg L^{-1})	Std. Dev.	Time(s) Sampled (PST)
14 Mile Slough	7.7	3.5	07/20/2004 13:00
Cosumnes River	24.3	7.2	07/18/2004 12:00
Georgiana Slough	3.3	1.1	12/12/2004 15:00
	3.6	0.8	12/12/2004 17:00
	22.4	4.6	03/16/2005 10:15
Frank's Tract	40.6	8.9	07/18/2004 12:00
Little Break	24.1	3.8	10/17/2005 13:51
	20.2	2.4	03/17/2005 15:15
	16.3	5.3	07/12/2005 09:50
Mandeville Bay	8.6	2.6	07/19/2004 12:00
	8.5	3.0	12/13/2004 13:35
	3.6	1.5	12/14/2004 15:00
	2.2	1.1	03/15/2005 12:30
	6.3	1.0	03/16/2005 16:30
	4.5	2.0	07/14/2005 18:00
	9.9	0.6	10/18/2005 09:30
	21.0	0.8	10/19/2005 14:45
Oakley Park	11.6	3.2	07/12/2005 12:15
	7.1	0.2	07/13/2005 14:30
	30.2	12.9	10/18/2005 14:56
	14.9	3.8	10/18/2005 20:35
	12.9	2.4	10/20/2005 09:22
Suisun Bay	4.7	2.2	07/20/2004 13:00
Sycamore Slough	1.5	0.6	12/12/2004 17:00

Figure 6 is a time series graph of DGM concentrations in Mandeville Cut, which had samples taken from it during every trip. The time is in Pacific Standard Time, and 0:00 hours represents midnight for each day. From such a wide time span and small number of samples, it is hard to make any definite assessments from figure 6. The small number of samples is due to the relatively long time required to analyze each sample. Figure 7 is a graph of DGM concentration sampled at three times between 10/18/2005 – 10/20/2005 for Oakley Park, i.e., morning (10/20/2005 09:22), afternoon (10/18/2005 14:56), and night (10/18/2005 20:35). The highest concentration was at the afternoon point (30.2 pg L^{-1}), which is consistent with the assessment of DGM concentrations being highest right after noontime (Amyot et al., 1994; Hines and Brezonik, 2004). However, this graph fails to present diurnal variations since DGM can undergo rapid concentration changes with time (O'Driscoll et al., 2003 a&b; 2006).

The average of the two samples (12.9 $\pm$ 6.9 pg L^{-1}) taken at 12:00 PST on March 16, 2005 at Georgiana Slough is reasonably close to the average of the continuous daytime (6:00 – 19:00 PST) samples (9.6 $\pm$ 4.7 pg L^{-1}) taken at the site a year later (03/31/2006 – 04/2/2006). This shows good agreement between the discrete and continuous techniques and also suggests that there is little probability of artifact (e.g. contamination, sample degassing) in the discrete system.
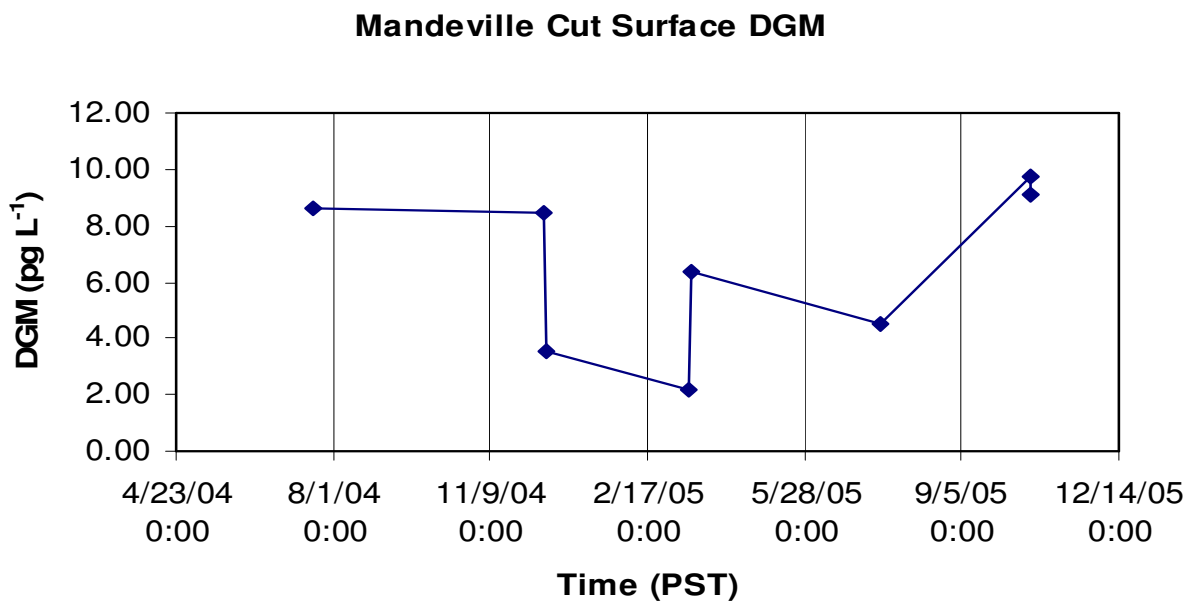
Mandeville Cut Surface DGM

Figure 6: Discrete DGM data collected from five CalFED trips for Mandeville Bay.

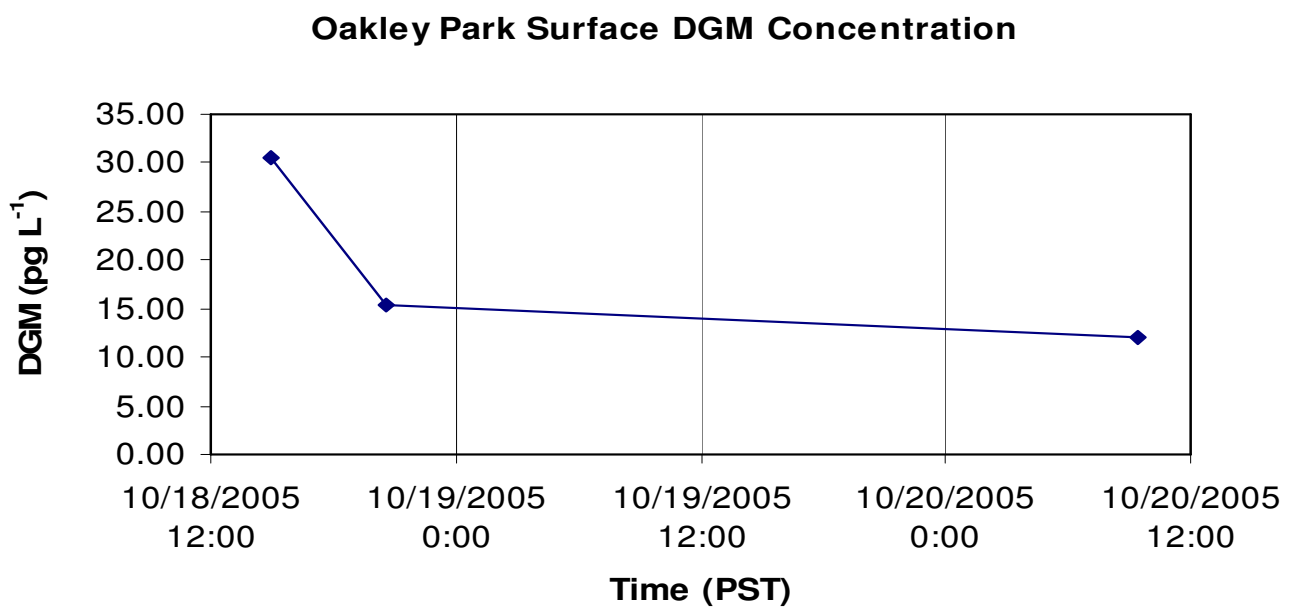**Oakley Park Surface DGM Concentration**

Figure 7: Discrete DGM data collected for Oakley Park.

Percent saturation data for the discrete samples can be seen in table 4. In the late spring and summer months, percent saturation is >100%, indicating super saturation. Under this condition, DGM is most likely to efflux from water to air (Mason et al. 1994; O'Driscoll et al. 2006; Poissant et al., 2000). In winter (Dec. 2004), the DGM concentrations were undersaturated (<100%). Also, during this time cloud cover was increased. This could have limited DGM photoproduction. Percent saturation seemed to be higher during the October 2005 trip. Also, the skies were clear during this trip. This coupled with intermediate temperature (16-18 $^\circ$C) allowed for maximum DGM photoproduction potential. Clear skies can be observed for the Bay-Delta area during summer (July) to late fall (October). Whereas increased cloud cover occurs from winter (December) to mid-spring (March). It is possible that cloud cover limits photoproduction which would decrease the saturation index in surface waters. Clouds block a portion of UV (a and b) light, which is a major controlling factor in DGM photoformation (Garcia et al., 2005; O'Driscoll et al., 2004).

Table 4: Table of saturation index (SI) for sample times and sites in the California Bay-Delta along with DGM concentration, surface temperature, and the temperature corrected Henry's Law constant (H').

Site	DGM (pg L^{-1})	Temp. (^{o}C)	H'	SI	Time(s) Sampled (PST)
14 Mile Slough	7.7	24.5	0.336	173.1%	07/20/2004 13:00
Cosumnes River	24.3	24.5	0.336	544.3%	07/18/2004 12:00
Georgiana Slough	3.3	12.1	0.245	53.0%	12/12/2004 15:00
	3.6	12.1	0.245	54.2%	12/12/2004 17:00
	22.4	15.5	0.270	403.1%	03/16/2005 10:15
Frank's Tract	40.6	24.5	0.336	544.3%	07/18/2004 12:00
Little Break	20.2	15.6	0.270	192.1%	03/17/2005 15:15
	16.3	23.9	0.332	532.4%	07/12/2005 09:50
	24.1	18.2	0.290	465.5%	10/17/2005 13:51
Mandeville Bay	8.6	24.5	0.336	193.8%	07/19/2004 12:00
	8.5	12.1	0.245	138.3%	12/13/2004 13:35
	3.6	12.1	0.245	58.2%	12/14/2004 15:00
	2.2	15.5	0.270	39.8%	03/15/2005 12:30
	6.3	15.5	0.270	114.0%	03/16/2005 16:30
	4.5	26.3	0.350	105.5%	07/14/2005 18:00
	9.9	17.6	0.285	174.5%	10/18/2005 09:30
	21.0	18.6	0.293	416.9%	10/19/2005 14:45
Oakley Park	11.6	22.9	0.325	225.3%	07/12/2005 12:15
	7.1	23.4	0.328	156.7%	07/13/2005 14:30
	30.2	18.5	0.292	664.3%	10/18/2005 14:56
	14.9	16.8	0.279	285.2%	10/18/2005 20:35
	12.9	17.3	0.283	212.4%	10/20/2005 09:22
Suisun Bay	4.7	24.5	0.336	104.3%	07/20/2004 13:00
Sycamore Slough	1.5	12.1	0.245	25.3%	12/12/2004 17:00

5.2 Continuous Analysis: Offatts Bayou, Texas vs. Georgiana Slough California

Figure 8 shows time series plots of surface temperature, dissolved oxygen, salinity, solar radiation, and DGM (continuous) for the March 2006 study of Offatts Bayou. The DGM concentration at Offatts Bayou for 3/15/2006 and 3/16/2006 followed a diurnal pattern with peaks occurring at mid-day (10am to 1pm CST). Dissolved oxygen and temperature also followed a diurnal pattern with peaks occurring around 4pm CST. Solar Radiation peaked at 3pm CST. The DGM peak occured before the solar radiation peak rather than after. This suggests that other processes besides light in the bayou are having a significant affect on the temporal DGM distribution. Usually, DGM responds after changes in light (time lag effect) rather than before, as has been noted in several other studies (Amyot et al., 1997b; da Silva et al., 2006; Hines and Brezonik, 2004; O'Driscoll et al., 2003 a&b). DGM concentrations appear to co-vary inversely with salinity here. This suggests that DGM concentrations at this time were somewhat influenced by chloride mediated oxidation. Chloride mediated oxidation should reduce the DGM pool in a system. Therefore, DGM should co-vary inversely with salinity. However, in the March study of Offatts Bayou, DGM showed no statistically significant correlation with D.O., temperature, or salinity (Pearson's correlation, $p>0.05$). Figures 9 and 10 show wind speed at 10 m height for all continuous studies. DGM did not correlate well with wind speed either. This is evident in figure 11.1. However, solar radiation data from Scholes did co-vary with DGM (Pearson's, $r = 0.451$, $p<0.05$). While the mechanisms for DGM production are still being explored, it is clear from the literature that solar radiation plays a major role (Amyot et al., 1994; Boudala et al., 2000; O'Driscoll et al., 2003 a&b; Zhang and Lindberg, 2001), as it was observed here.
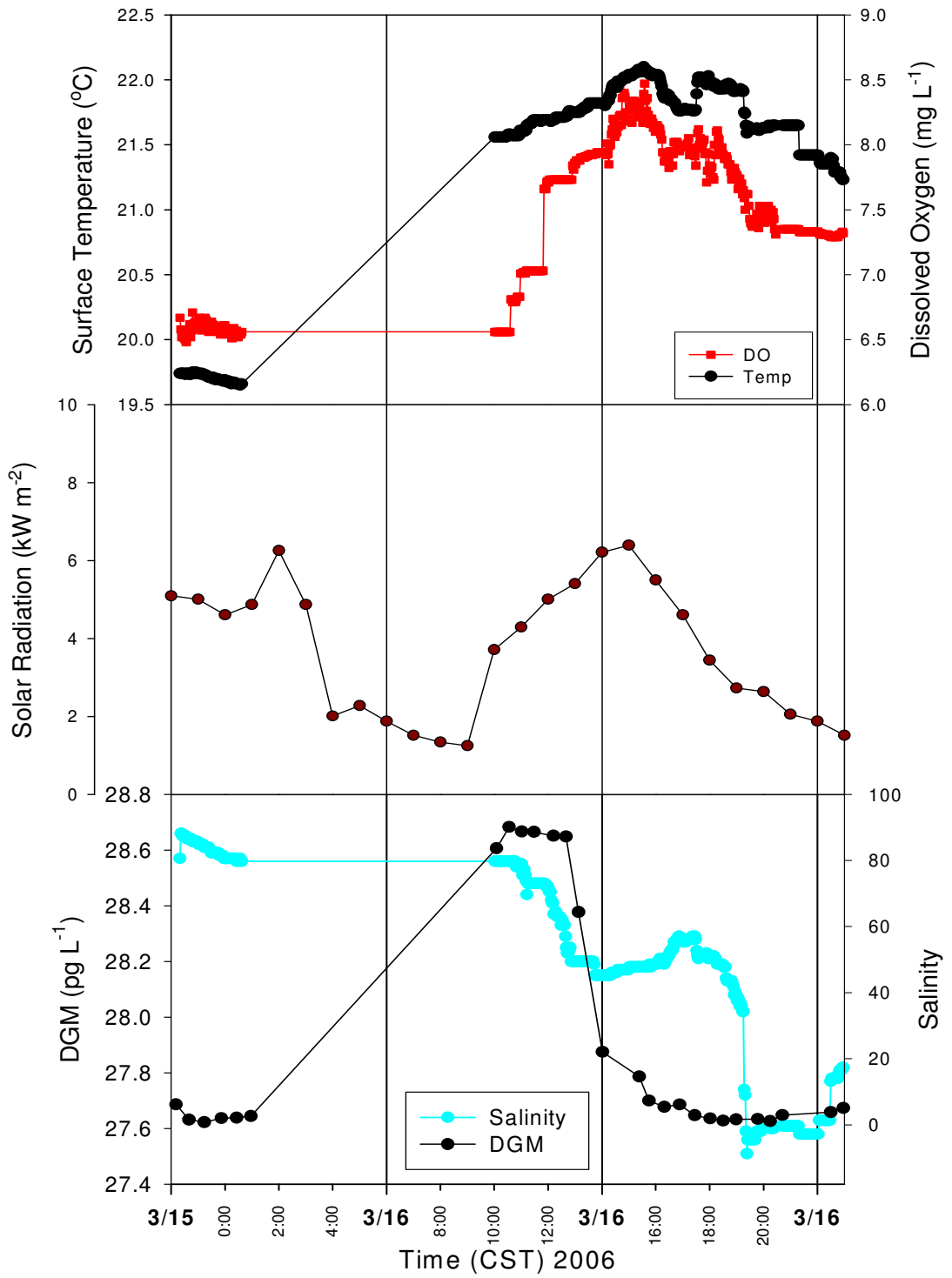
Figure 8: Continuous DGM analysis of Offatts Bayou, Texas.

The link to dissolved oxygen and DGM may be the result of sunlight induced biological processes that affect DGM production directly (Siciliano et al., 2002). All statistical results for the different correlations can be found in table 5.

The average concentration for the continuous measurement for March at Offatts Bayou (25.3 $\pm$ 8.8 pg L^{-1}) was greater than the average at the California site (Georgiana Slough) in March (9.6 $\pm$ 6.6 pg L^{-1}). This average at Offatts Bayou is somewhat lower than values found in the literature covering salt water systems (44.1 $\pm$ 16.0 pg L^{-1} for Amyot et al., 2000; 40.1 $\pm$ 26.1 pg L^{-1} for Rolfhus and Fitzgerald, 2005). The average DGM found at Georgiana Slough is somewhat lower than values found in literature for freshwater sites: 46.3 pg L^{-1} in O'Driscoll et al. (2003a) and 35.3 pg L^{-1} in Poulain et al. (2004). The difference in average DGM concentrations between the March Offatts Bayou study and the Georgiana Slough study could be due to the fact that it was overcast most of the time in California and clearer skies at Offatts Bayou in March during the times of measurement. According to the paired samples t-test, Offatts Bayou had more solar radiation than Georgiana Slough at the times of measurement ($p<0.05$, t=2.356). This could explain why Offatts Bayou, on average, had higher DGM concentrations than Georgiana Slough. For the Georgiana Slough data (figure 12), DGM correlated significantly with dissolved oxygen (Pearson's, r = 0.485, $p<0.05$) and temperature (Pearson's, r = 0.612, $p<0.05$). Salinity was less than 0.1 for Georgiana Slough. DGM also co-varied with winds at this site (figure 11.2, Pearson's, r = 0.603, $p<0.05$). The PAR data shifted back one hour correlated quite well with the DGM concentrations at Georgiana Slough (Pearson's, r = 0.854, $p<0.05$).

Therefore, it is probable that DGM concentrations are influenced mostly by PAR, wind, temperature, and dissolved oxygen at the Georgiana site for the month of March. Time shifted solar radiation components (e.g. PAR, UV a and b) have been found to correlate well with DGM concentration data. O'Driscoll et al. (2003 a&b) have determined that DGM photoformation can take up to 90 minutes to complete. The correlation with dissolved oxygen suggests that biological activity could be influencing DGM concentration. The wind speeds for Offatts Bayou can be seen in figures 9-10. The wind speeds vary diurnally like DGM concentrations with maximum values occurring at midday (12 – 2 P.M.). Wind speed correlated positively with solar radiation for the March Offatts Bayou study (Pearson's, r = 0.566, p<0.05). Wind speed positively correlated with PAR in the May (Pearson's, r = 0.451, p<0.05) and August studies (Pearson's, r = 0.499, p<0.05). This indicates that DGM and winds are controlled by sunlight and covary as a result.

Table 5: Pearson's correlation coefficients between DGM and other parameters for the continuous studies. X's indicate that there was no significant correlation between DGM and the parameter.

Offatts Bayou 03/15/2006 – 03/16/2006

Parameter:	D.O.	Temperature	Salinity	U_{10}	Solar Radiation
DGM	X	X	X	X	0.451

Georgiana Slough 03/31/2006 – 04/02/2006

Parameter:	D.O.	Temperature	Salinity	U_{10}	PAR	PAR_{-1hr}
DGM	0.485	0.612	X	0.603	X	0.854

Offatts Bayou 05/17/2006 – 05/18/2006

Parameter	D.O.	Temperature	Salinity	U_{10}	PAR	PAR_{-1hr}
DGM	0.498	0.723	-0.632	0.472	X	0.701

Offatts Bayou 08/16/2006 – 08/17/2006

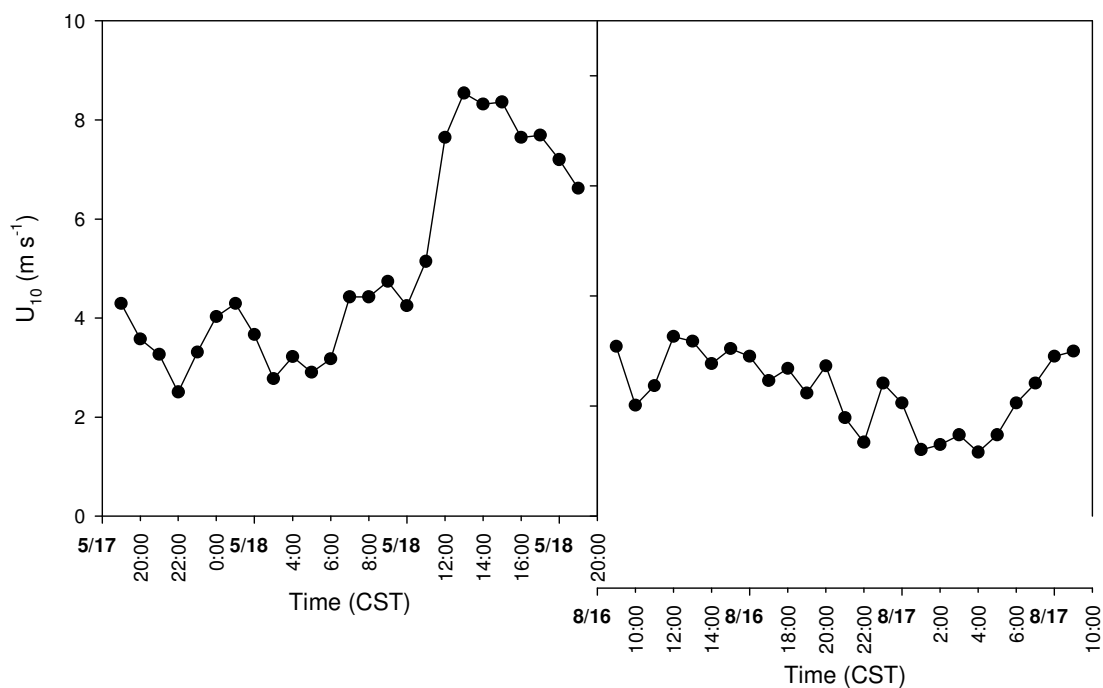| **Parameter**	D.O.	Temperature	Salinity	U_{10}	PAR	$PAR_{-1\ hr}$
DGM	0.500	0.462	-0.544	0.450	X	0.705

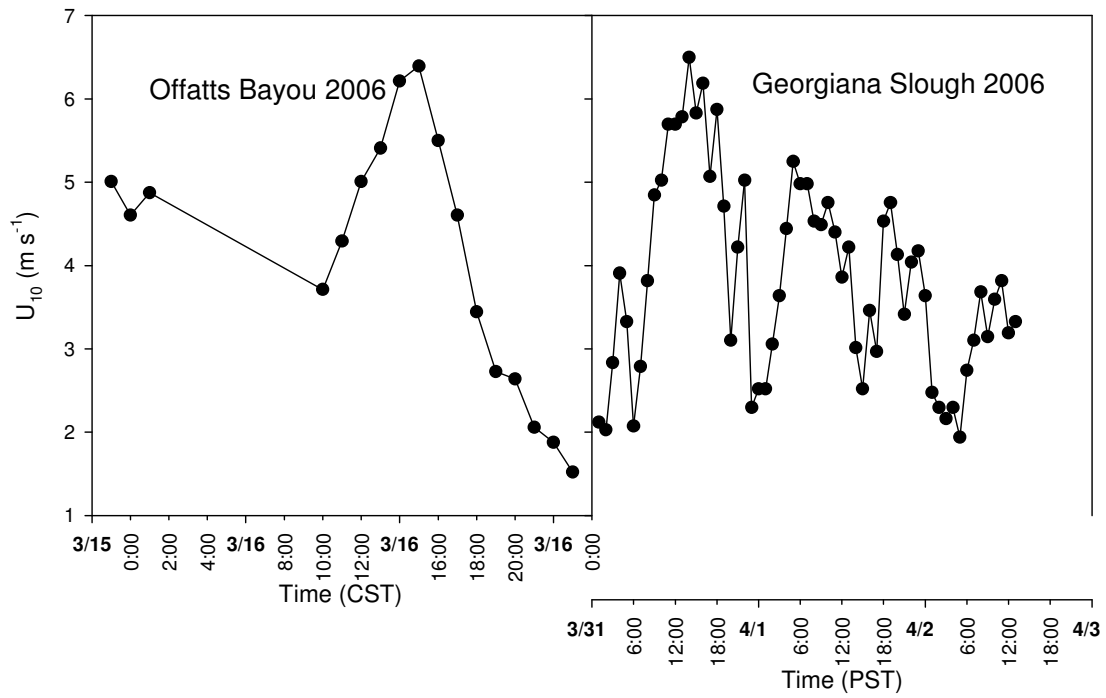**Figure 9: Wind speed at 10 m height for Offatts Bayou 2006.**

Figure 10: Wind speed at 10 m height for Offatts Bayou and Georgiana Slough.
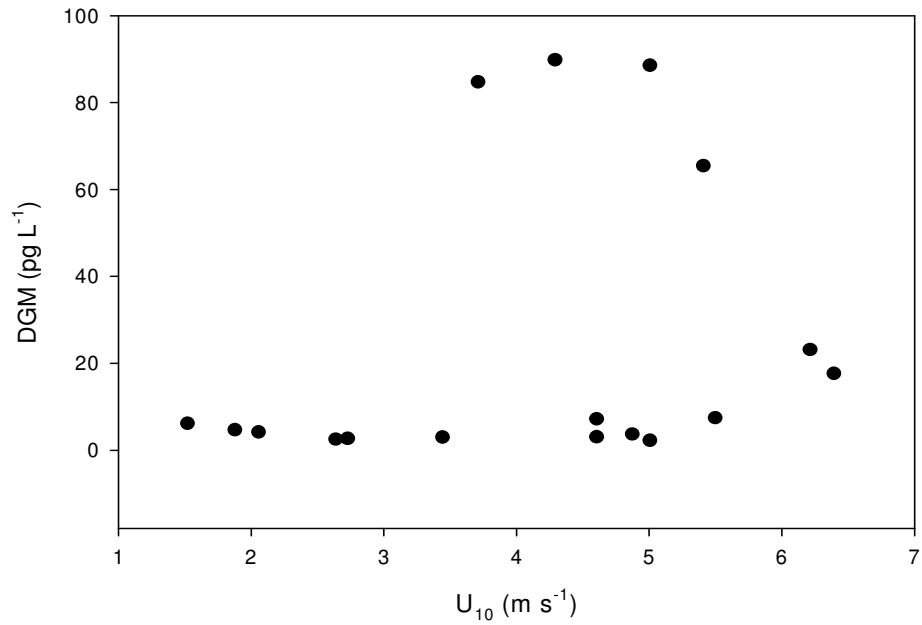
Offatts Bayou March 2006

Figure 11.1: DGM vs. U10 for Offatts Bayou March 2006. DGM did not correlate with wind for this study (Pearson's, r = 0.112, p>0.05).
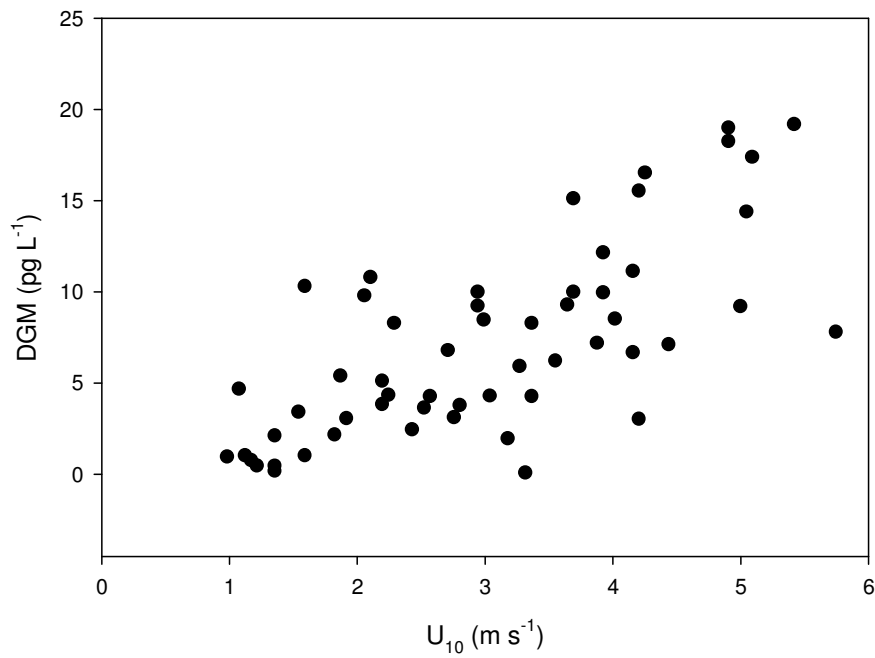
Georgiana Slough 3/30/2006 - 4/2/2006

Figure 11.2: DGM vs. U10 for Georgiana Slough March-April 2006. DGM did correlate well with wind for this study (Pearson's, r = 0.714, p<0.05).

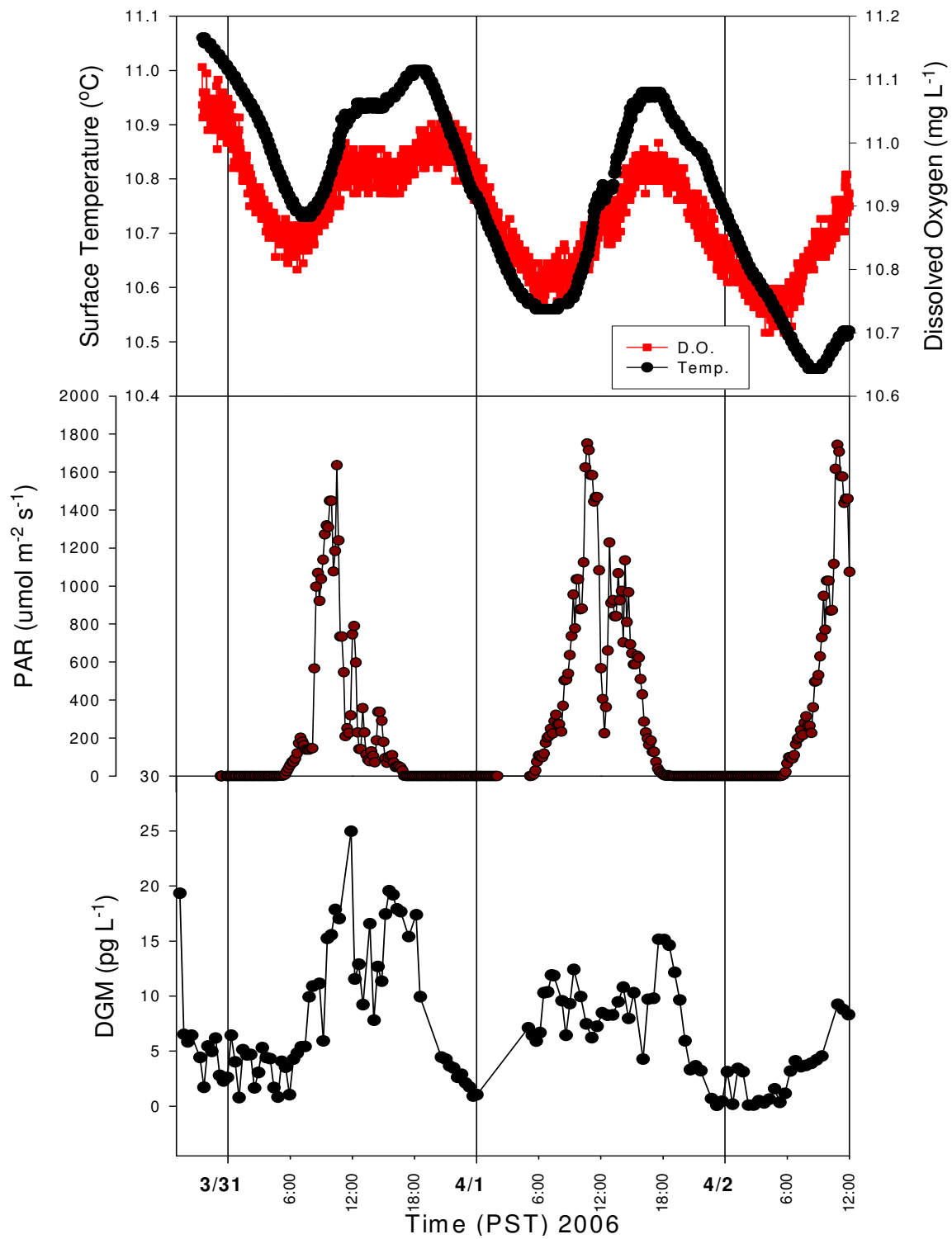**Figure 12: Continuous DGM analysis of Geogiana Slough, California.**

5.3 Flux Models

Three flux models were used to predict air-water elemental mercury exchange. A constant value of 1.5 ng m^{-3} was used for the atmospheric concentration of elemental mercury. This the average gaseous elemental mercury value observed by Dr. Key-Young Choe of the Laboratory for Oceanographic and Environmental Research in both the Galveston Bay region and San Francisco Bay-Delta region (unpublished data). Figures 13-16 show time series DGM concentrations and fluxes for each continuous study. The Schroeder et al. (1992) model does not consider wind speeds in the K_w calculations, whereas the Poissant et al. 2000 model does. However, the Poissant et al. (2000) model is only reliable for $U_{10} < 5$ m s^{-1}. Most wind speeds in this study (~90%) were less than 5 m s^{-1}, so this model was suitable for use. Wind speeds for all three Offatts Bayou studies and the Georgiana Slough study can be seen in figures 9-10. The Schroeder et al. (1992) flux model is considered the most reliable for these studies because of a lack of an available anemometer on site. Also, authors who have measured the DGM flux have shown that the Schroeder et al. (1992) model correlates better with measured DGM flux values than when using other predictive flux models (Hines and Brezonik 2004, O'Driscoll et al. 2003 a&b, Garcia et al. 2005). I found no significant difference between the Poissant et al. model (2000) and the Schroeder et al. model (1992) for all four continuous studies (paired samples t-test, p>0.05, t=2.312).

The Schroeder et al. (1992) model flux for the March study at Offatts Bayou at 12:00

noon is 36.1 pmol m^{-2} h^{-1}. This is reasonably close to 25.6 pmol m^{-2} h^{-1} for Long Island

Sound in Rolfhus and Fitzgerald (2001). The Boudala et al. (2000) model gives

significantly higher DGM fluxes than the Poissant et al. (2000) and the Schroeder et al.

(1992) models (paired samples t-test, p<0.05, t=1.689). This can be seen on figures 13-

16 as well. However, the Boudala et al. (2000) model time shifted back one hour was

significantly correlated to DGM concentration (Pearson, r = 0.708, p<0.05). This gives

validity to the Boudala et al. (2000) model in this study since it was developed for lakes

in the Canadian shield. It has also been shown that factors other than wind and solar

radiation can influence DGM fluxes (Amyot et al. 2000, Garcia et al. 2005). The fluxes

given by the Schroeder et al. (1992) model for the March Offatts Bayou study were twice

those at Georgiana Slough on average. This is possibly due to the increased cloud cover

during sampling time at Georgiana Slough (March) as opposed to clear skies at the time

of sampling for Offatts Bayou (March).

Figure 13: The DGM concentration and flux values predicted by three different models for the continuous March study of Offatts Bayou, Texas.

Figure 14: The DGM concentration and flux values predicted by three different models for the continuous March study of Georgiana Slough, California.
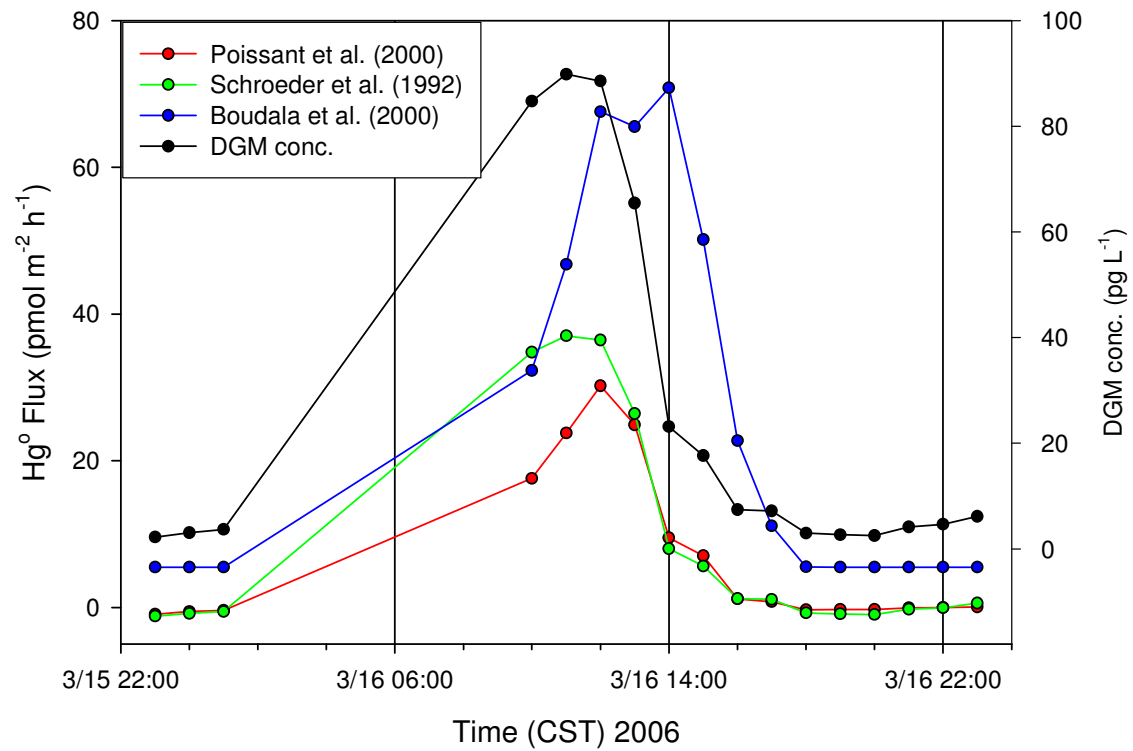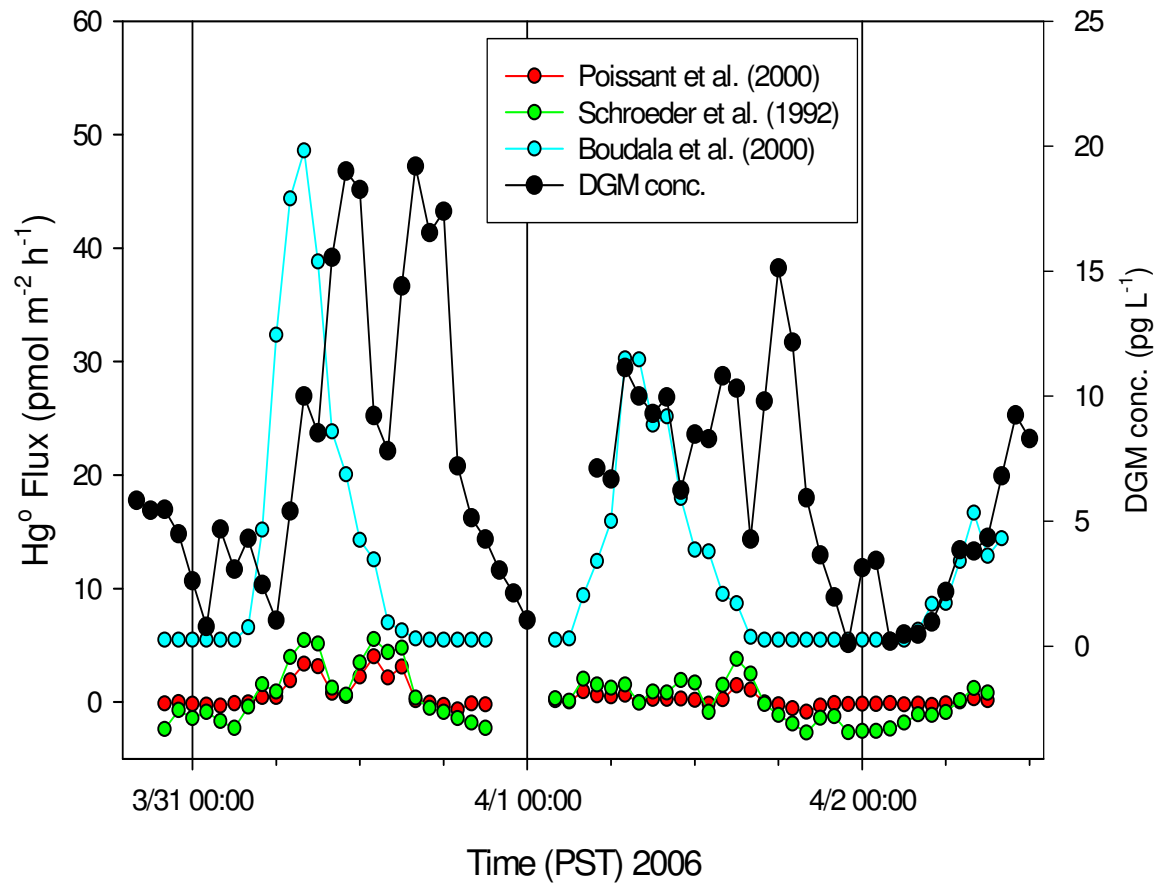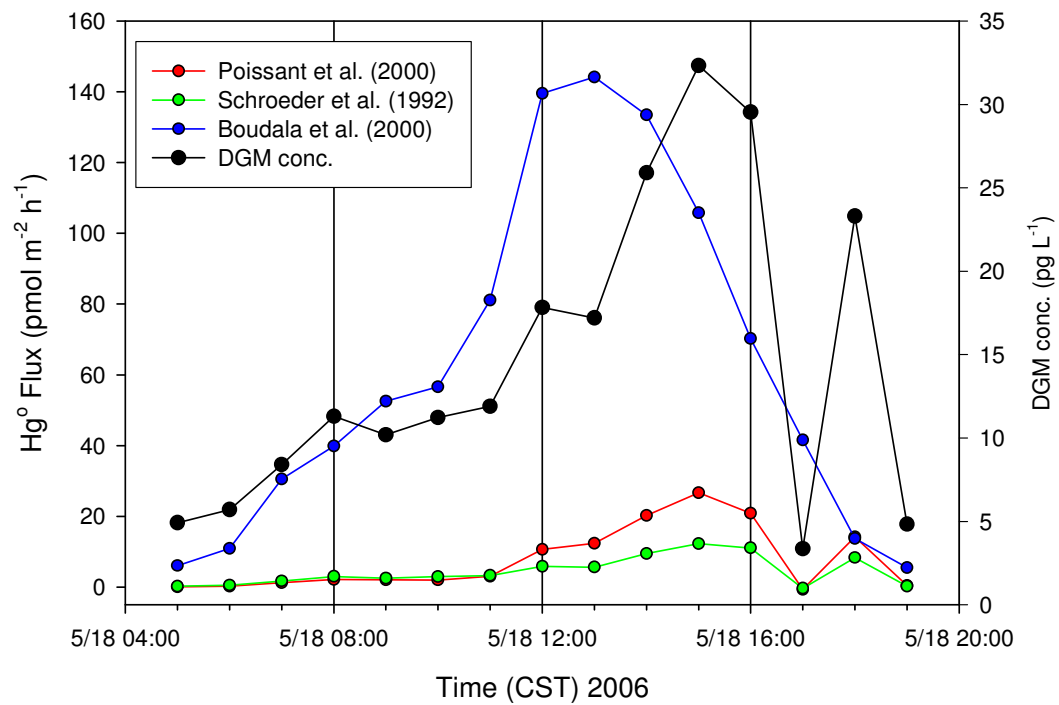
Figure 15: The DGM concentration and flux values predicted by three different models for the continuous May study of Offatts Bayou, Texas.
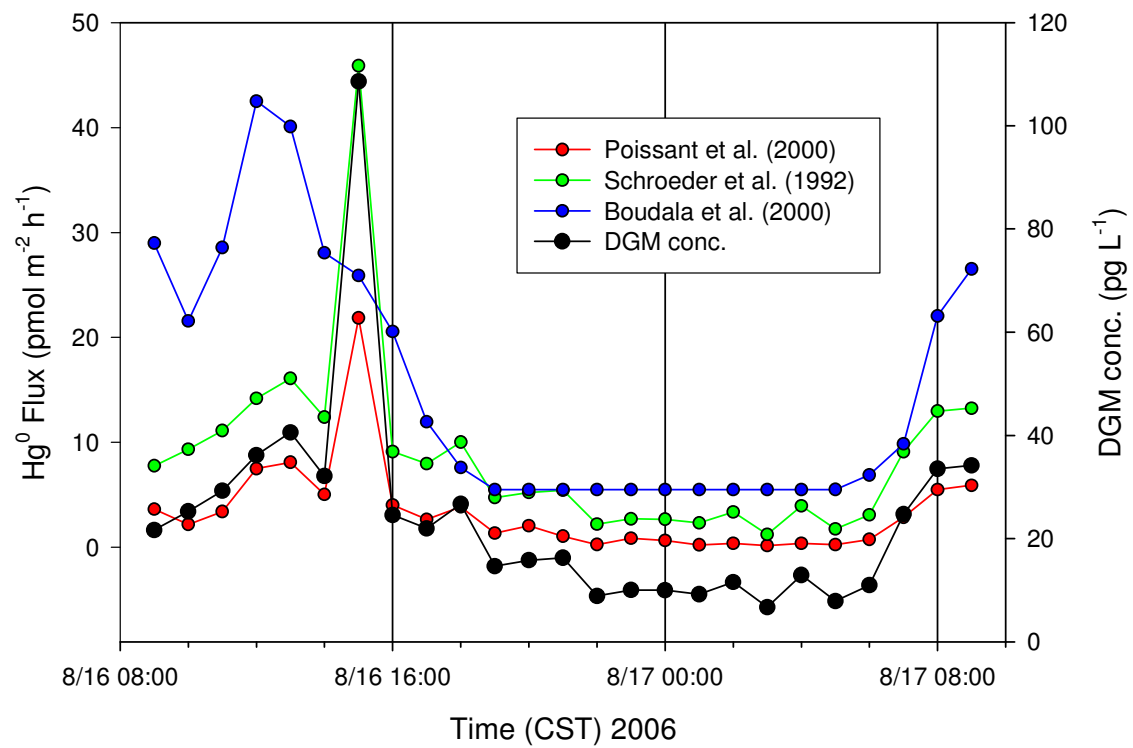
Figure 16: The DGM concentration and flux values predicted by three different models for the continuous August study of Offatts Bayou, Texas.

5.4 Discrete DGM Analysis in Offatts Bayou

Figures 17-19 show DGM, salinity, dissolved oxygen, and temperature depth profiles at Offatts Bayou for six trips made between 7/29/2005 and 6/30/2006. Discrete samples in OB show similar surface concentrations to those made in continuous modes. The average of the late spring concentrations for discrete surface sample is 29.6 pg L^{-1} in morning for the June 30, 2006 profile. In the continuous analysis May study (figure 23), the average DGM concentration for late morning (9 am – 11 am) was 32.5 pg L^{-1}. The two different techniques were close in value. This suggests that the discrete samples in Offatts Bayou had little artifact (i.e. no DGM loss from degassing).

DGM concentrations decreased slightly with depth and co-varied inversely with salinity. Figure 20 shows all six depth profiles of DGM. There is no significant correlation between DGM and depth. The problem could be that one would have had to sample more depth intervals in order to observe spatial trends. However, the long processing time of samples coupled with an unknown DGM loss rate from the sample bottle did not allow it to take more depth samples.

A significant correlation was found between DGM and salinity (Pearson's correlation, $p < 0.05$, $r = -0.541$). However, DGM did not correlate with dissolved oxygen or temperature.

Figure 21 shows a biological activity profile in terms of total chlorophyll A. It can be clearly seen that biological activity increased in late spring and was lowest in winter (November). Summer was highly stratified in terms of D.O., winter profiles were more mixed in terms of D.O. (especially in Feb profile). Conversely, biological activity increased in deep waters (7-9m) from winter to late spring, even though dissolved oxygen concentrations were highest at 7-9m in late winter months (Jan. and Feb.) DGM was correlated to total chl A slightly (Pearson's, $r = 0.203$, $p < 0.05$), as seen in figure 22. It is possible that DGM was controlled somewhat by biological processes. Another possibility is that DGM and biomass (total chl A) were controlled by a mutual parameter, such as sunlight intensity. Hence, sunlight intensity would cause of DGM and biomass to covary. This has also been proposed by Poulain et al. (2004).

Figure 17: Depth profiles of DGM, salinity, temperature, and dissolved oxygen for the July 2005 and November 2005 studies.   **The points are mean concentration while the error bars represent one standard deviation.**
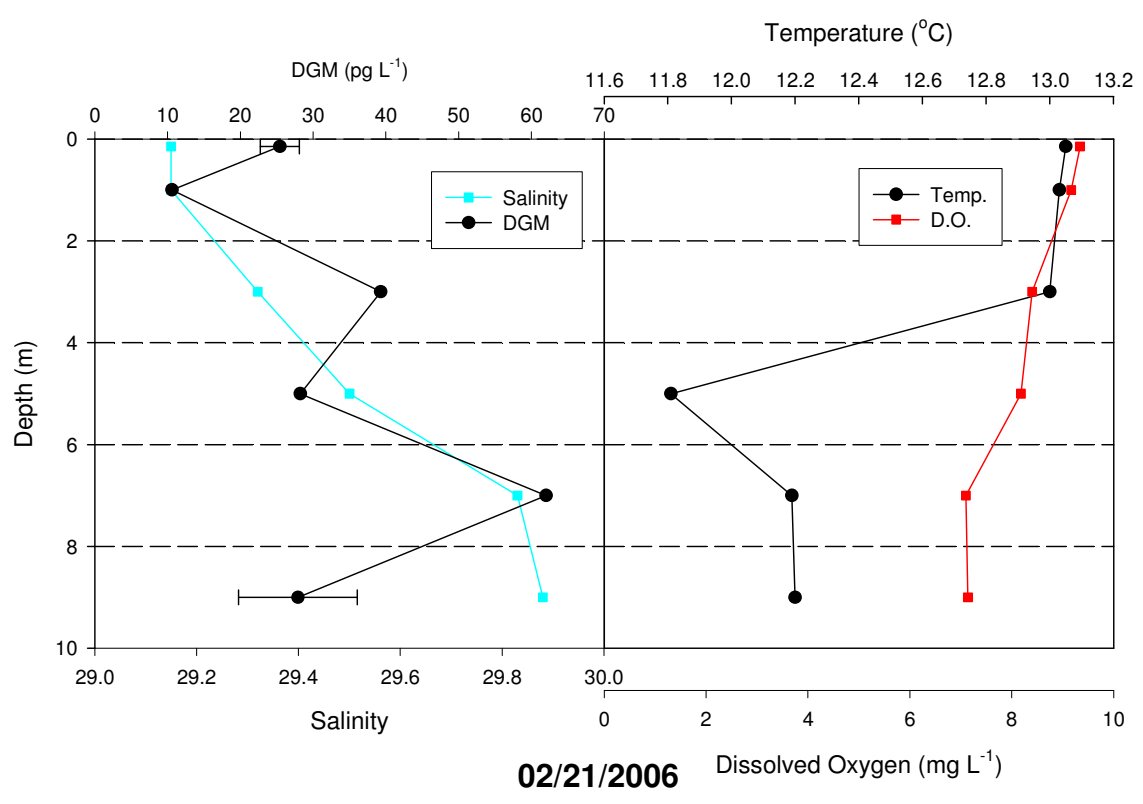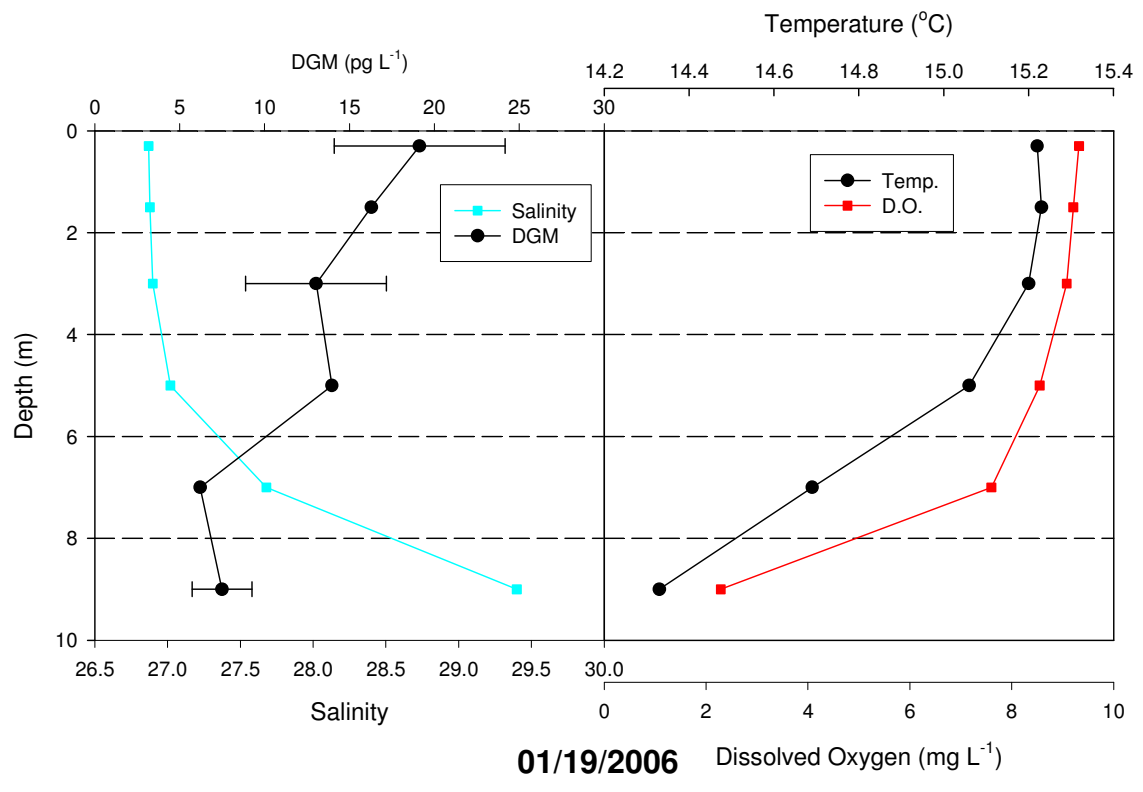
Figure 18: Depth profiles of DGM, salinity, temperature, and dissolved oxygen for the January 2006 and February 2006 studies. The points are mean concentration while the error bars represent one standard deviation.
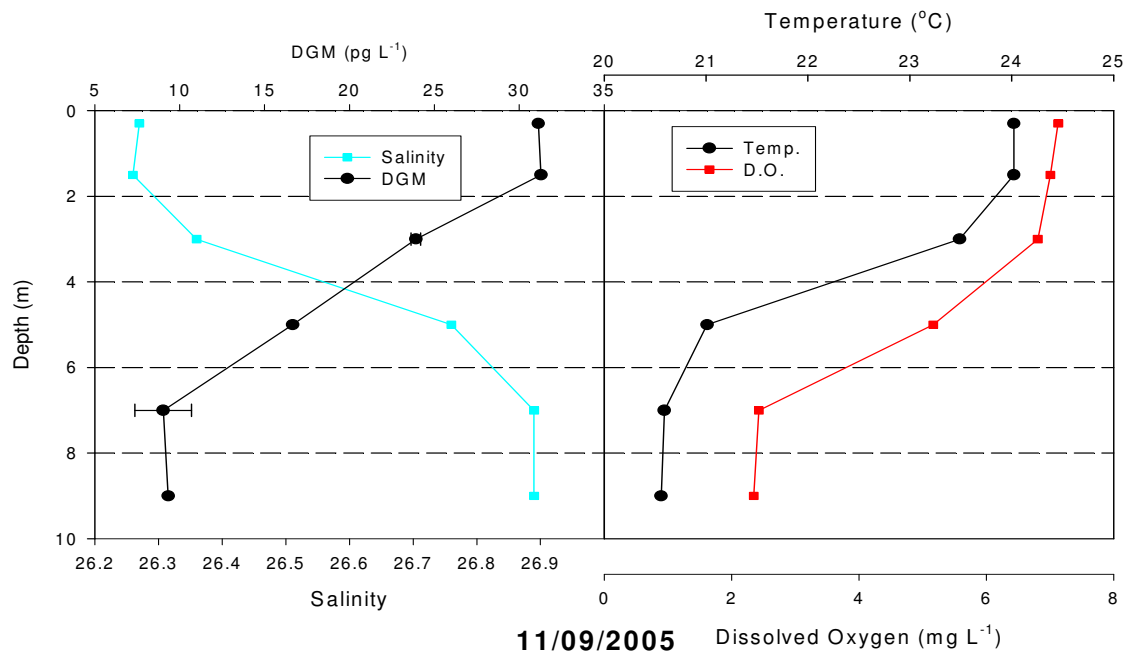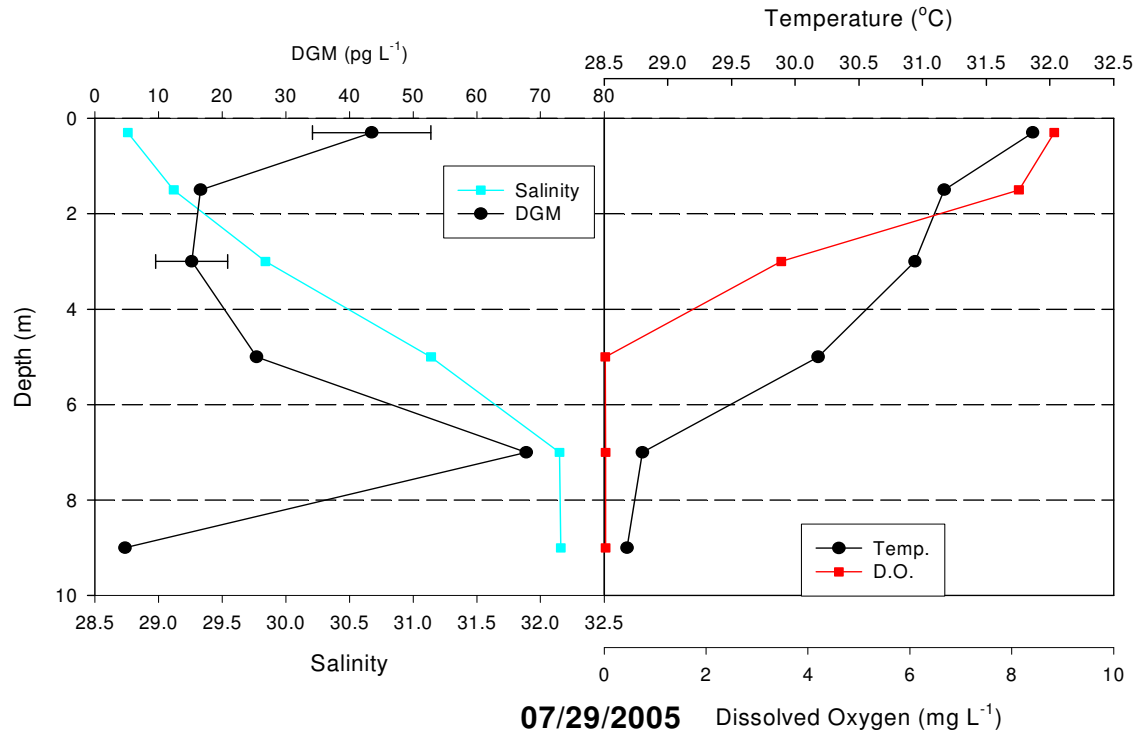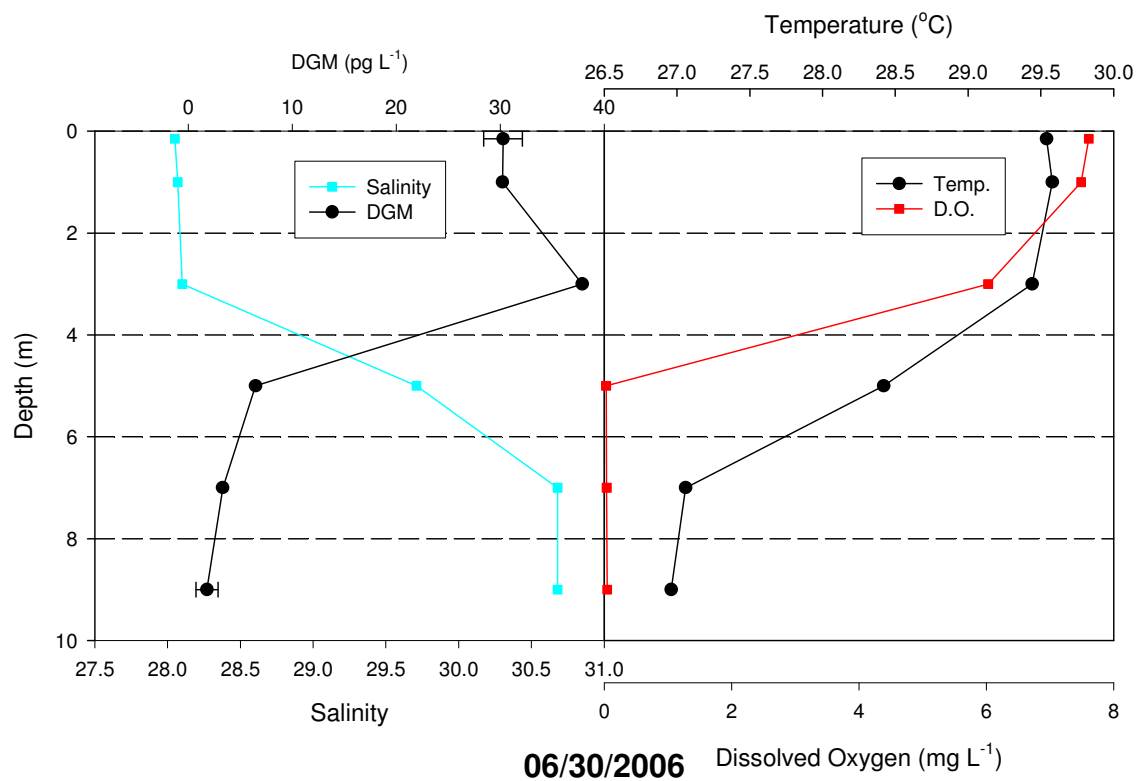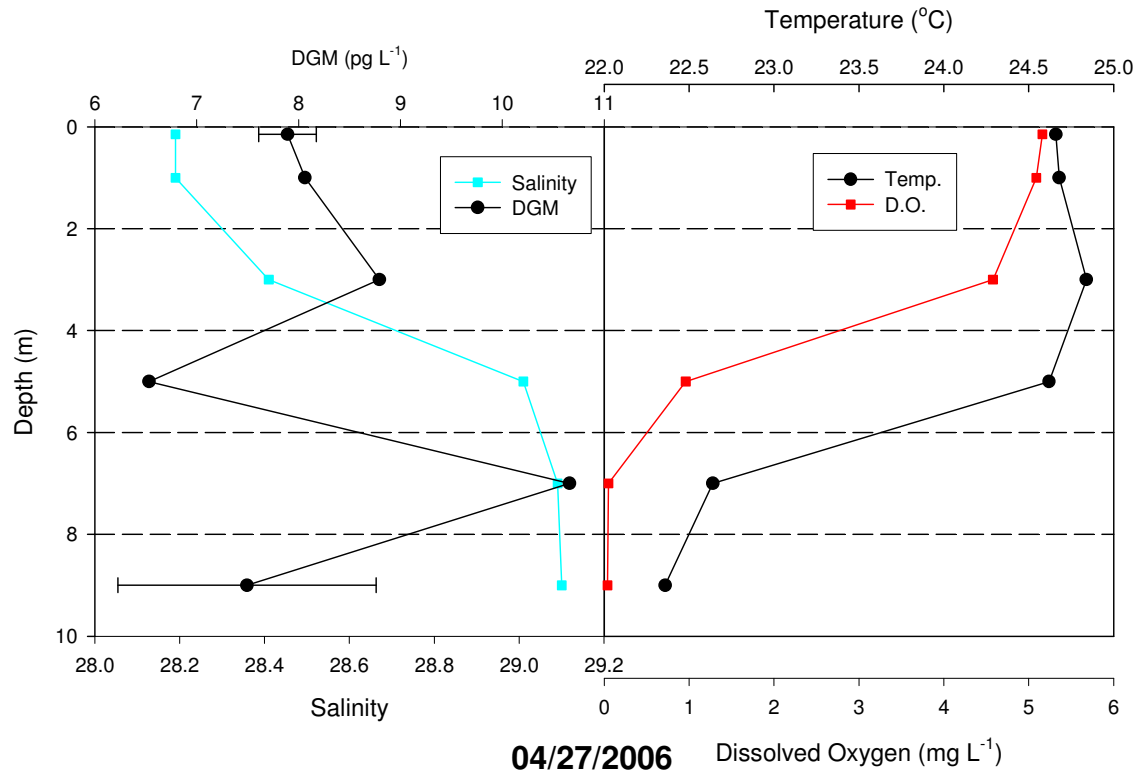
Figure 19: Depth profiles of DGM, salinity, temperature, and dissolved oxygen for the April 2006 and June 2006 studies. The points are mean concentration while the error bars represent one standard deviation.
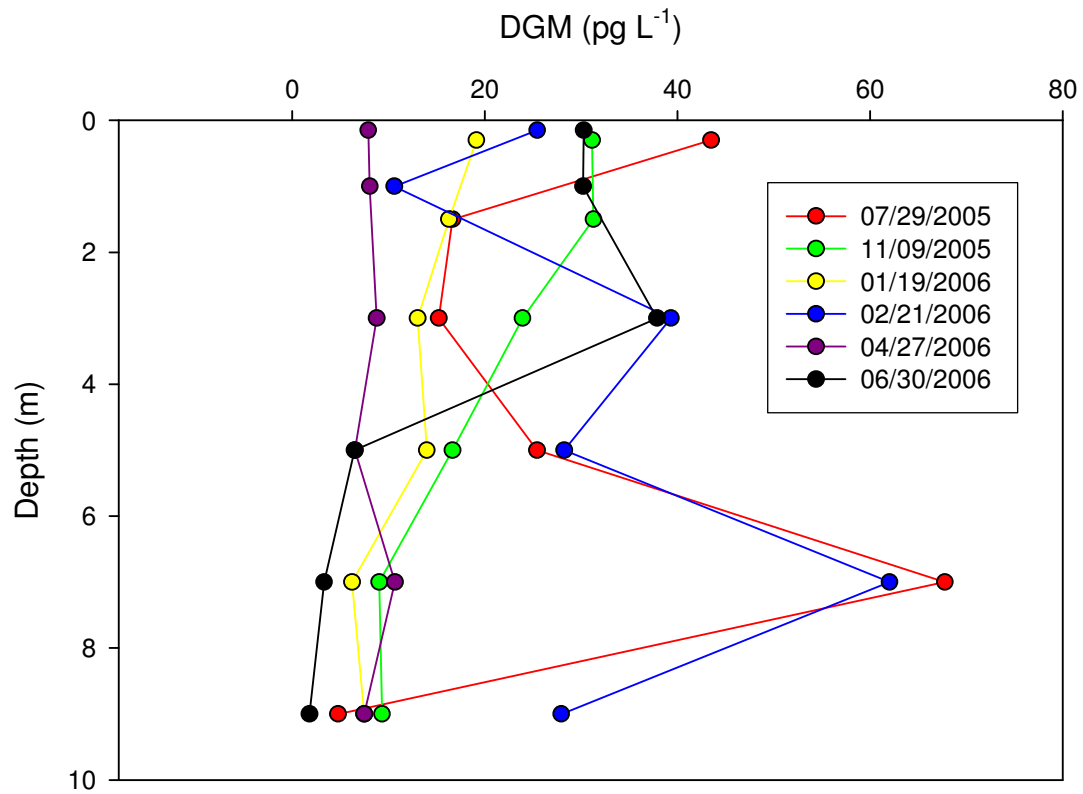
Figure 20: DGM Depth profiles for all studies conducted at Offatts Bayou.
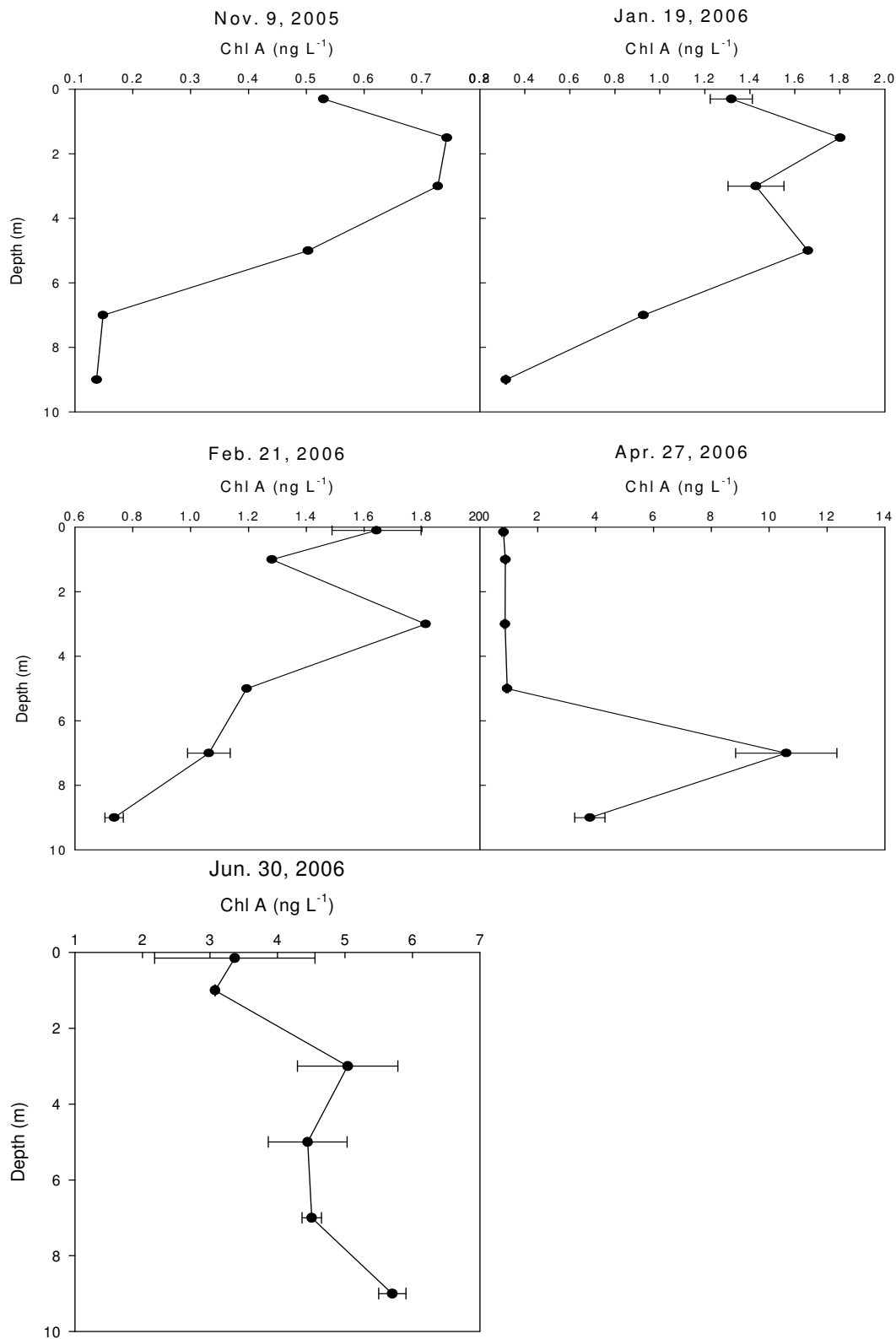
Figure 21: Total chlorophyll A concentration profiles at Offatts Bayou. Points with error bars indicate duplicate samples taken at depth. The points are mean concentration while the error bars represent one standard deviation.

DGM vs. Total Chl A (biomass) for all Offatts Bayou Depth Profiles
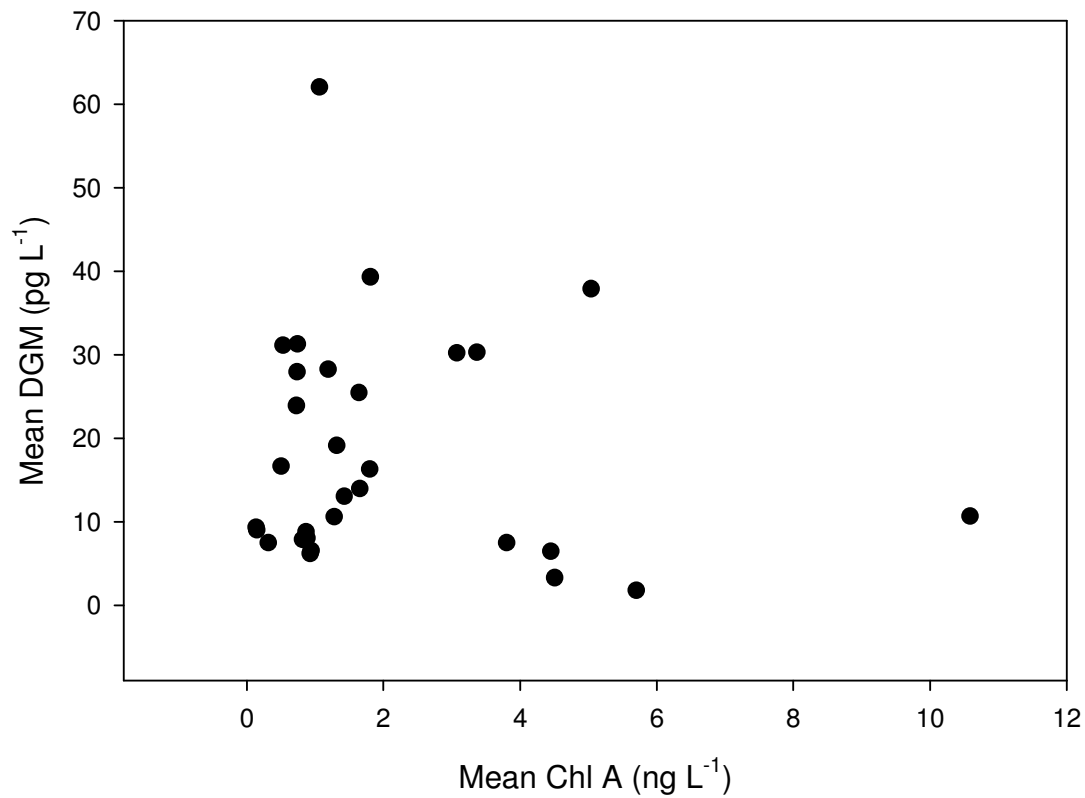
Figure 22: Mean DGM (of replicates) vs. mean Chl A concentration for all Offatts Bayou depth profiles. A slight correlation was found between chl A and DGM concentration with Pearson's test (r = 0.203, p < 0.05).

5.5 May Offatts Bayou Continuous Study

Time course measurements of the DGM concentration at Offatts Bayou for

5/17/2006 – 5/18/2006 (Figure 23) also followed a diurnal pattern, as did temperature and

DO. Dissolved gaseous mercury diurnal patterns for DO, temperature, and DGM

followed a similar pattern. There appeared to be a time lag in the time course

measurements between PAR, DO, DGM, and temperature. This suggests that

photochemistry dominates DGM production here as photochemical reactions take time to

complete (Dill et al., 2005; O'Driscoll et al., 2006). The DGM maximum at mid-day

(30.2 pg L^{-1}) was lower than the maximum in March (85 pg L^{-1}). Winds were also

calmer, as higher wind speeds can enhance water to air transfer of DGM. DGM

concentrations were significantly correlated to wind speed (Figure 24, Pearson's, r =

0.472, p<0.05). Winds were much stronger during the March trip, thus enhancing the

potential for increased water to air DGM transfer. DGM did correlate with salinity

(Pearson's, r = -0.632, p<0.05). DGM also correlated with PAR (r = 0.701), dissolved

oxygen (r = 0.498), and temperature (r = 0.723) when PAR values were shifted back one

hour. This implies that DGM photoreductions took one hour to complete.

Figure 23: May continuous study of Offatts Bayou. Time series plots of DGM, salinity, D.O. temperature, and PAR.

Offatts Bayou May 2006

Figure 24: DGM vs. U10 for Offatts Bayou May 2006. DGM did correlate well with wind for this study (Pearson's, r = 0.472, p<0.05).

5.6 August Continuous Study of Offatts Bayou

Time course DGM concentrations in Offatts Bayou for 8/16/2006 – 8/17/2006 (Figure 25) also followed a diurnal pattern, as does temperature and dissolved oxygen. DGM diurnal patterns for dissolved oxygen, temperature, and DGM follow a similar pattern. Once again, there appears to be a time lag in the patterns between PAR, dissolved oxygen, DGM, and temperature. DGM concentrations were significantly correlated to winds (Figure 26, Pearson's, $r = 0.450$, $p<0.05$), salinity (Pearson's, $r = -0.544$, $p<0.05$), PAR ($r = 0.705$), dissolved oxygen ($r = 0.500$), and temperature ($r = 0.462$) when PAR values were shifted back one hour. Trends and correlations observed for DGM in August were very similar to that observed in May for Offatts Bayou. The daily maximum for both studies occurred at about 15:00 (3:00 PM).
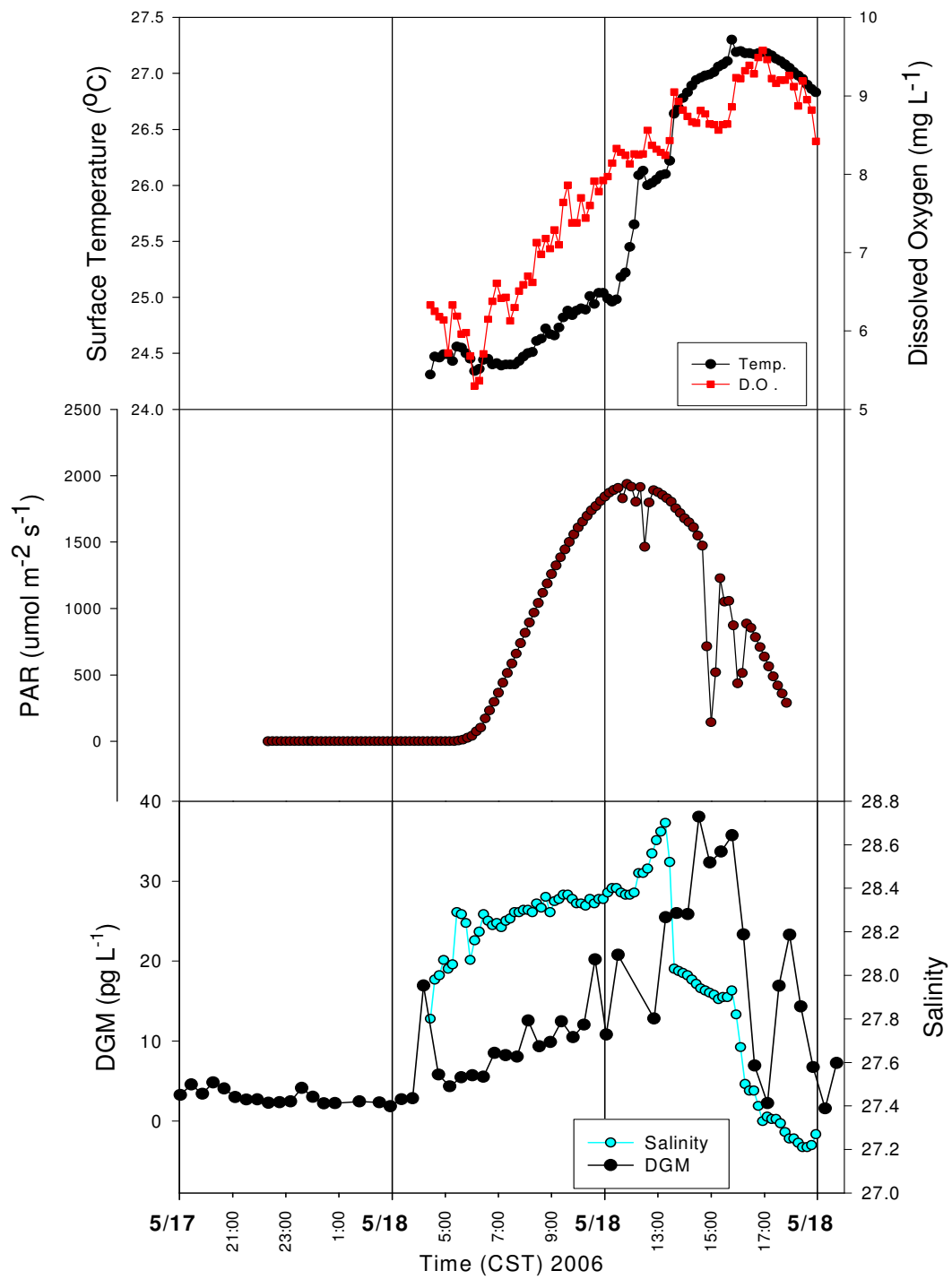
Figure 25: August continuous study of Offatts Bayou. Time series plots of DGM, salinity, D.O. temperature, and PAR.
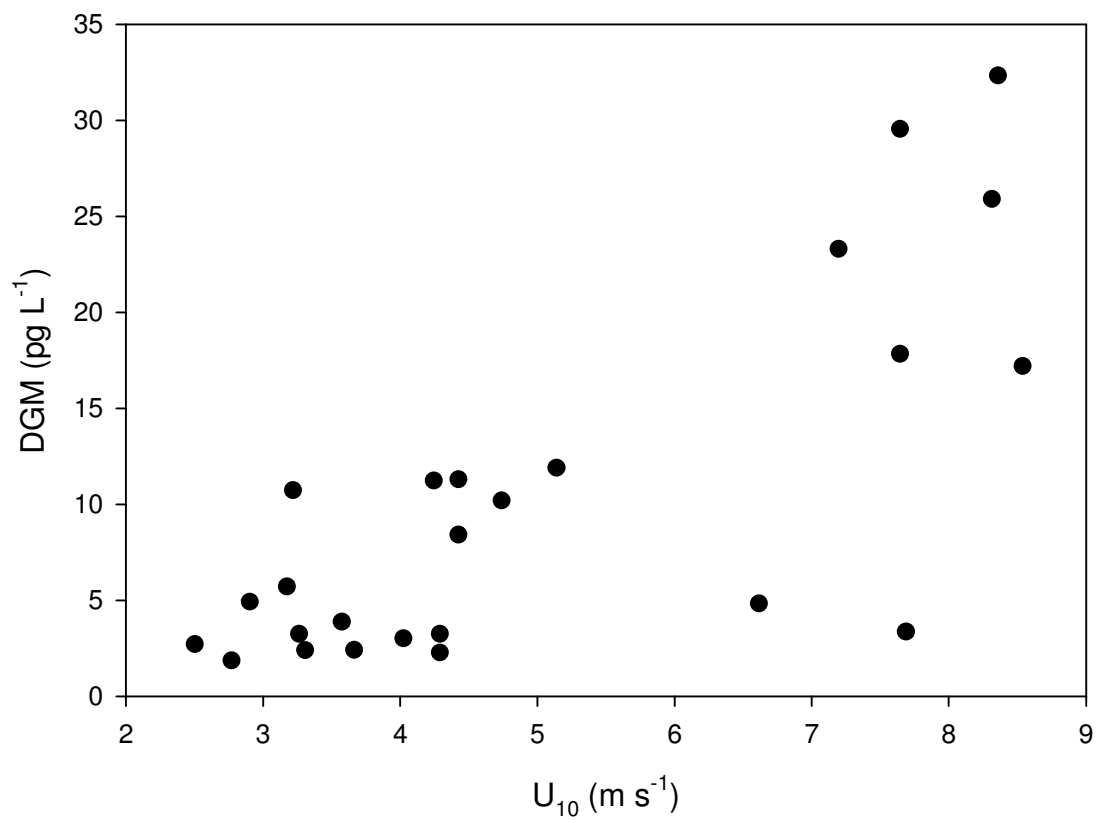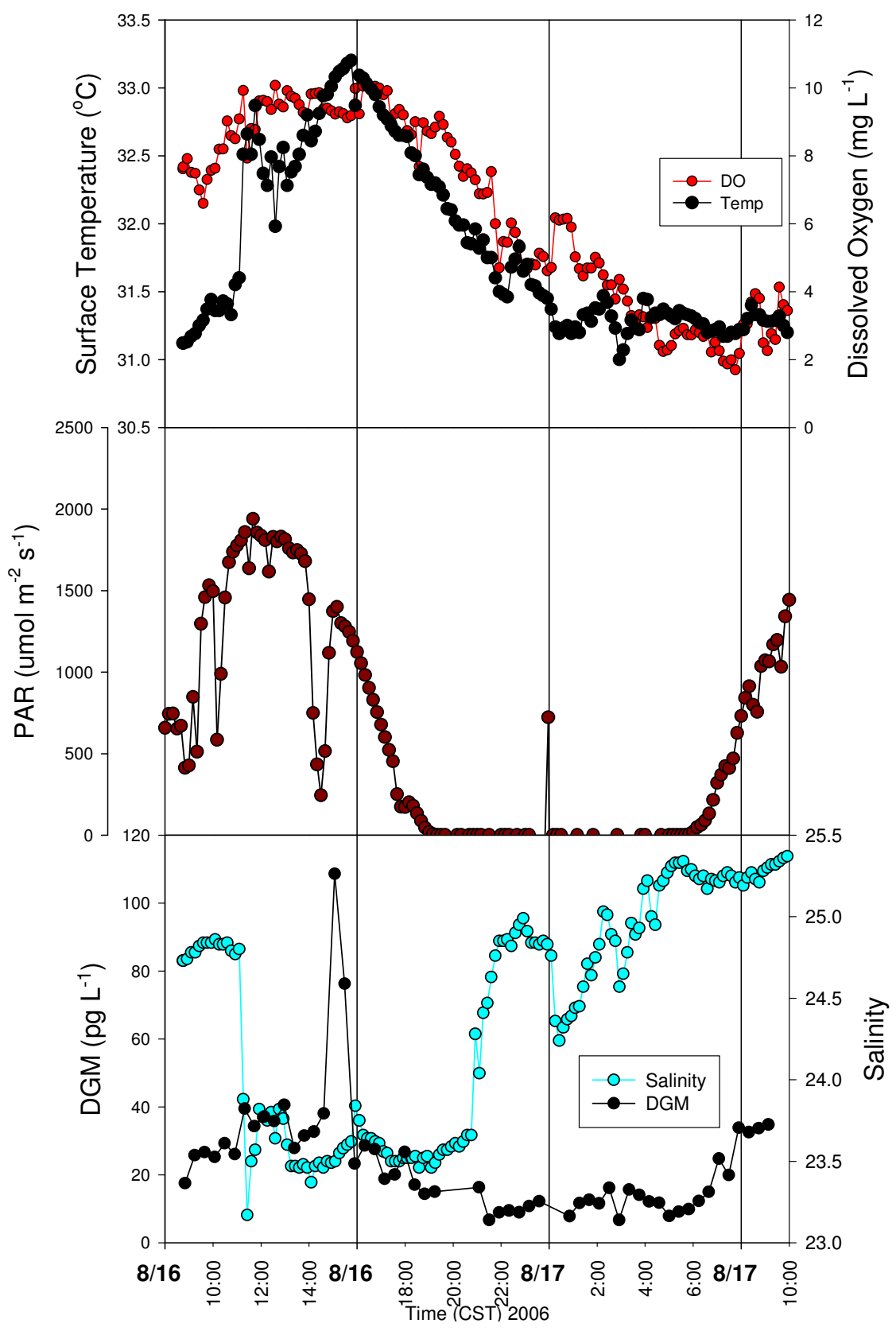
Offatts Bayou August 2006
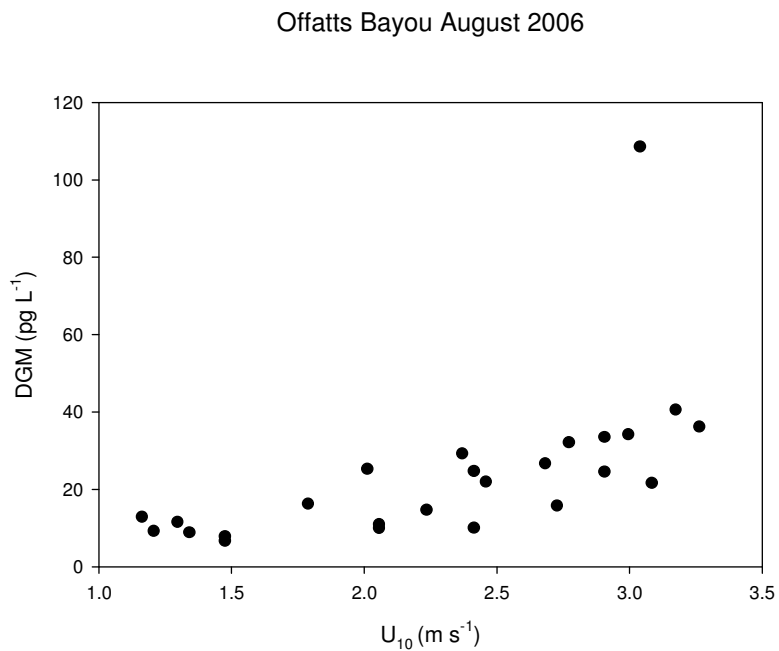
Figure 26: DGM vs. U10 for Offatts Bayou August 2006. DGM did correlate with wind for this study (Pearson's, r = 0.450, p<0.05).

6. SUMMARY AND CONCLUSIONS

Dissolved gaseous mercury was measured in two different types of estuarine environments and with two different methods, discrete and continuous analysis. The discrete technique is time consuming (~2 hr from sample collection to analysis). Even though the technique works reasonably well and is reproducible (Amyot et al., 1997b; Hines and Brezonik, 2004; O'Driscoll et al., 2003 a&b), it does not allow one to observe rapid changes in DGM concentration that can occur in as little as 20 minutes (O'Driscoll et al., 2003a). The discrete sampling technique agreed well with the continuous technique for both Offatts Bayou and Georgiana Slough. During the development of the continuous analysis system, several discrete samples were collected in the California Bay-Delta in order to refine the discrete technique.

The March study of Offatts Bayou had a significantly higher DGM concentration than Georgiana Slough California. At Georgiana Slough, there was enhanced cloud cover during the entire sampling session. The average DGM concentration for the Offatts Bayou March study was higher than for Georgiana Slough in California. This is likely due to clearer skies, and thus higher solar radiation, during the Offatts Bayou sampling period.

The hypothesis tested was that DGM exhibits temporal and spatial trends and is affected by several environmental parameters. DGM seemed to correlate the best with solar radiation (and PAR) data. Many authors agree that sunlight reactions are the driving force behind DGM cycling (Amyot et al., 1997b; da Silva et al., 2006; Garcia et al., 2005; O'Driscoll et al., 2003 a&b). Also, when the Poissant et al. (2000) and the Schroeder et al. (1992) predictive flux models were applied to the data, the flux dropped

to zero or below during night time. This suggests that the flux potential is heavily dependent on sunlight. While sunlight is a major factor in DGM cycling and distribution, the mechanism of sunlight induced DGM transformation is not well known, even though there have been many experiments to assess the rate of photo-transformation of DGM. Boudala et al. (2000) and O'Driscoll et al. (2003 a&b) found that photoreactions take about an hour to complete. However, sunlight transformations do cause rapid changes in DGM concentration in short periods of time. In this study, DGM concentrations increased by as much as five times between mid-morning and early afternoon.

Another major controlling factor of DGM is wind speed. The flux models of Poissant et al. (2000) and Boudala et al. (2000) make use of wind speed at 10 m height in the piston velocity (K_w) calculation. This is because of wind affecting the shape of the diffusive boundary layer. As a result, the higher the wind speed, the more water to air transfer will occur, thus resulting in a negative correlation between DGM and wind speed. Conversely, a positive correlation between wind and DGM was found for every continuous study except for the March continuous study.

Salinity does correlate negatively with DGM for the May and August Offatts Bayou continuous studies, indicating the possibility of chloride mediated oxidation. This has been proposed previously in several studies (Costa and Liss, 1999; Lanzillota et al., 2001; Yamamoto, 1996). Temperature co-varies with DGM positively for the Georgiana Slough and May and August Offatts Bayou studies. Not much has been said in the literature about the effects of temperature on DGM (Lin and Tao, 2003). Dissolved oxygen varies positively with DGM for the Georgiana Slough and May and August Offatts Bayou studies. Some authors suggest that dissolved oxygen is an indicator of

biological activity that may be influencing DGM concentrations (Poulain et al., 2004; 2007).

The profiles in Offatts Bayou provided some interesting results, but the data set is not large enough to reach definite conclusions. For instance, it was not clear if DGM was influenced by depth. DGM also did not correlate with dissolved oxygen or salinity, as was expected. But DGM did correlate positively with total chlorophyll A. It is possible DGM is controlled biologically with increasing depth. It would have been better to take 10 sampling depths for the Offatts Bayou study. Since discrete samples take so long to analyze and the DGM loss rate from sample bottles is unknown, it was not a practical approach. Utilizing the continuous system for the depth profiles would have been helpful.

Nonetheless, this study does contribute much to the understanding of DGM cycling in aquatic environments as there are few studies that incorporate continuous analysis DGM techniques like the one used in this thesis (O'Driscoll et al., 2003 a&b; O'Driscoll et al., 2006; Rolfhus and Fitzgerald, 2001). However, it is difficult to make any definite assessments about seasonal DGM variations with the continuous data because the data were collected in spring and summer. A winter data suite for both Georgiana Slough and Offatts Bayou would have been helpful. However, due to funding and time constraints, it was not possible.

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VITA

Charles Melchor Landin received his Bachelor of Science in Marine Sciences with honors at Texas A&M University at Galveston on May 2003. He is currently pursuing a career with SGS Oil, Gas, and Chemical. He may be reached by phone at 713-857-6942 or email at cmlandin@sbcglobal.net. His department address is LOER Lab 5007 Avenue U Galveston, TX 77550.