MERCURY SOURCES AND CYCLING PROCESSES IN THE CAPE FEAR RIVER
ESTUARY, NORTH CAROLINA

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ABSTRACT

SUZANNE ZVALAREN SCHNEIDER: Hg Sources and Cycling Processes in the Cape Fear
River Estuary, North Carolina
(Under the direction of Joan D. Willey)

This research presents the first data on mercury (Hg) concentration and speciation in

North Carolina for a southeastern US blackwater estuary. Water column data for Hg

speciation and ancillary parameters were determined on 11 cruises between July 2004 and

September 2006. Average surface water concentrations for total dissolved Hg (TDHg) were

7 pM and ranged from <1 to 37 pM, while the average particulate Hg (Hg$_{part}$) concentrations

was 11 pM with a range of <1 to 46 pM. Average methylmercury (MeHg) surface water

concentrations were 0.42 pM and ranged from <0.1 to 1.7 pM. TDHg concentrations are

highest under medium flow conditions, where as Hg$_{part}$ concentrations are highest under high

flow conditions.

Sediment analyses throughout the estuary revealed elevated concentrations of Hg at

freshwater stations M61, HB and LVC.   Hg concentrations are similar throughout the lower

estuary when normalized to organic carbon content, however concentrations at LVC are

elevated suggesting a local point source from a defunct chlor-alkali plant. Benthic flux

experiments conducted at M61 and HB indicate that sediments act as both a source and sink

for total Hg in the estuary, having one of the highest TDHg flux out of sediments in

comparison to other estuaries. However, sediments were never a source of MeHg in the

Cape Fear River estuary (CFRE) unlike many other systems where sediments are a

significant input of MeHg to overlying waters.

Photolysis experiments indicate that irradiation of CFRE water does not impact the speciation or concentration of water column TDHg. Photolysis of estuary water containing ambient particles and resuspended bottom sediments show no clear increase or decrease of water column Hg concentrations. Irradiation of unfiltered CFRE surface waters produces significant concentrations of dissolved gaseous Hg (DGHg) and demethylates Hg at a rate dependent on initial MeHg concentration.

Mass balance calculations indicate that riverine input is the primary source of Hg and MeHg to the estuary. The primary sink for TDHg is benthic flux. Tidal exchange transports approximately 20% of total Hg and 40% of MeHg to the coastal ocean. Comparison with other estuaries indicates that the CFRE is a moderately impacted industrialized estuary.

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Chapter 1 – General Introduction

Rationale

The distribution and reactivity of mercury (Hg) in the environment is of great importance because some of the transformations that occur lead to the increase of toxic Hg species. In North Carolina, as in many locales throughout the world, anthropogenic Hg releases occur through various point sources, including electric utility plants, industrial boilers, medical, hazardous, and municipal waste incineration, and manufacturing processes. Natural sources of Hg include coal, volcanoes, rocks and minerals.

Several species of fish in North Carolina have elevated levels of Hg in various waterbodies east of I85. An area of concern in southeastern North Carolina is the potential contamination of the lower Cape Fear River watershed by the former HoltraChem Corp plant. The 24 acre plant is located on the banks of the Cape Fear River in Columbus County and is surrounded by International Paper. The HoltraChem facility was in operation from 1963 to 1999 as a chlor-alkali manufacturing plant that utilized the Hg cell process. The plant was constructed to provide chlorine gas, caustic soda and bleach to the International Paper facility. Process water from HoltraChem was discharged and housed in lagoons on the banks of the Cape Fear River. The plant ceased operations in 1999, however, until 2008 a large quantity of elemental Hg (~17.5 tons) remained within the factory and lagoons near the river contained ~11 million liters of Hg-contaminated liquid waste.

The EPA issued a memorandum in July 2002 for a time critical removal of Hg from the HoltraChem site. Removal of the waste began in January 2003 removing Hg cells from

the buildings and other potentially hazardous materials. Complete removal of hazardous materials from the former HoltraChem site was to be completed by December 31, 2008   The plant site is currently listed as a hazardous waste (Superfund) site in the USEPA Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) because of Hg contamination. CERCLIS is a national database used by the EPA to monitor activities at hazardous waste sites under the Superfund Act. CERCLIS contains the official inventory of Superfund sites and supports EPA's site planning and tracking functions.

Hg contamination of aquatic resources including economically important fish species is a chronic problem in many coastal areas. There are currently 10 consumption advisories in North Carolina for specific water bodies in addition to a statewide coastal consumption advisory. The EPA reports that in 2005, 158 new fish advisories and 162 previous advisories were reactivated in the United States (EPA, 2007). Elevated levels of MeHg (MeHg) were found in fish tissues, including those of bowfin and largemouth bass, at numerous stations throughout the Cape Fear watershed, including the mainstem river, and the Northeast Cape Fear and Black Rivers. Due to MeHg bioaccumulation, fish consumption advisories exist for blackfish, bowfin, chain pickerel, and largemouth bass in all North Carolina waters and for king mackerel, shark, swordfish, and tilefish in the Atlantic Ocean from the North Carolina/South Carolina border to Cape Hatteras.

There are currently no high quality data on Hg concentration or speciation in the waters of the Cape Fear River Estuary system despite previous data documenting significant Hg contamination. In addition to the paucity of data pertaining to concentration and speciation of Hg, there is no information regarding the processes that control its behavior or

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ultimate fate once it enters the watershed. This research presents the most comprehensive data set on Hg speciation and cycling in a southeastern blackwater estuary as well as the first water column data for the Cape Fear River estuary.

Background

Hg is both a naturally occurring element and a pervasive environmental contaminant. Hg enters the environment by a variety of natural and anthropogenic sources. Natural sources include volcanoes, coal, rocks and minerals. Anthropogenic sources include chlor-alkali plants, coal combustion, waste incinerators, metal smelting and emissions from cement plants. Hg is primarily released in to the atmosphere as gaseous Hg (Hg^o). Hg^o is very stable and has a half life of 0.5 to 2 years in the atmosphere (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999). Therefore Hg^o is unreactive with low water solubility and a long atmospheric residence time, once released it can travel long distances from its original source and affect areas that would otherwise not be influenced by the emission of Hg. Particulate Hg and divalent Hg (Hg^{2+}) are less stable in the atmosphere and are mainly emitted by anthropogenic sources (Selin and Jacob, 2008). Their atmospheric residence times are days or weeks. Hg is primarily deposited by wet deposition as Hg^{2+}. The deposition of divalent Hg to land and water bodies introduces a particle reactive, highly soluble species of Hg to environments where potential transformations may alter the speciation and bioaccumulation of Hg in natural environments.

Estuaries provide a link in the biogeochemical cycling of Hg between the terrestrial environment and the oceans (Mason et al., 1994; Fitzgerald and Mason, 1997; Mason et al., 1999). Hg exists in three forms in estuarine environments: elemental Hg (Hg^o), divalent inorganic Hg (Hg^{2+}) and MeHg (CH_3Hg^+), abbreviated as MeHg. The dynamic estuarine

environment has the potential to provide many pathways for the transformation between Hg species found in marine environments. Of greatest importance is the methylation of divalent Hg, as MeHg, because it is the toxic form that bioaccumulates and biomagnifies in nearshore environments (Baeyens et al., 2003; Hammerschmidt and Fitzgerald, 2006). The bioaccumulation of MeHg increases exposure to humans because the primary source of exposure is consumption of contaminated fish.

Study Location

Cape Fear River Estuary

The Cape Fear River is a highly turbid, darkly colored, light limited, partially mixed estuary. The Cape Fear River watershed is about 23,696 square kilometers and is the most heavily industrialized watershed in North Carolina with 244 permitted wastewater discharges and (as of 2000) over 1.83 million people residing in the basin (NCDENR 2005). The watershed drains the lower one-third of the state and contains about 25% of the state's population. The estuary is located between the cities of Wilmington and Southport along the southeastern coast of North Carolina (Figure 1.1) and has been extensively monitored for water quality since 1995 by the Lower Cape Fear River Program (LCFRP). The LCFRP currently encompasses 36 water sampling stations throughout the Cape Fear, Black, and Northeast Cape Fear River watersheds. The LCFRP sampling program includes physical, chemical, and biological water quality measurements (Mallin et al., 2007).

The Cape Fear system has a deep, dredged river channel (~15 m) and is characterized by large inputs of organic substances from upstream freshwater swamps and two blackwater tributaries (Black River and Northeast Cape Fear River) (Shank et al., 2004b; Shank et al., 2004a). The Atlantic Ocean as well as the Atlantic Intracoastal Waterway contributes

Figure 1.1 Map of the Cape Fear River estuary showing all sampling stations.
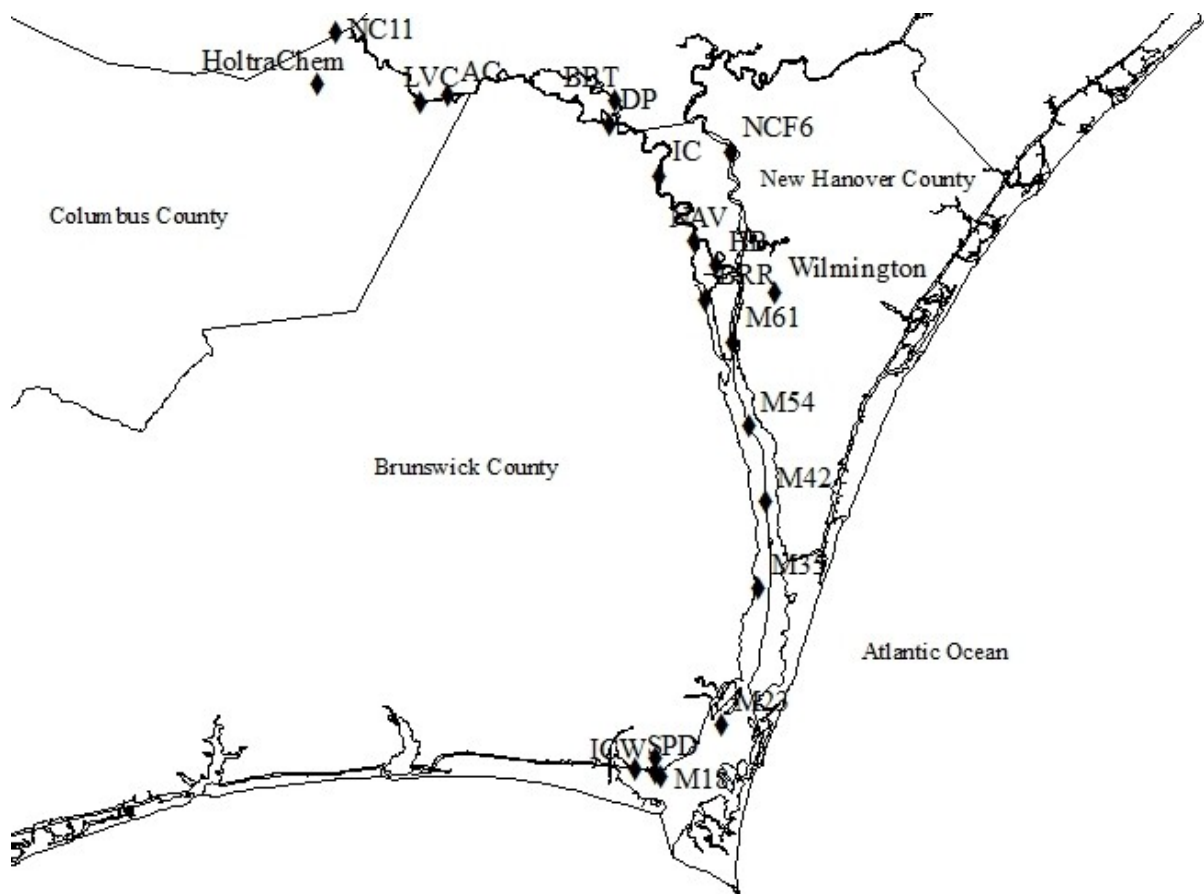
seawater to the lower estuary. Dissolved organic carbon concentrations range from 200 to 1200 μM C (Avery et al., 2003). The Cape Fear River estuary is a well-flushed system, with flushing time ranging from 1 to 22 days with a median flushing time of about seven days, much shorter than the other large North Carolina estuaries (Ensign et al., 2004).

Research Objectives

1. Determine the concentration and speciation of Hg in the Cape Fear River Estuary.

2. Evaluate the benthic flux of dissolved Hg and MeHg in the Cape Fear River Estuary.

3. Evaluate the photochemical processes that may affect Hg speciation and concentration in the Cape Fear River Estuary.

4. Evaluate the impact of sediment resuspension events on water column concentration and speciation of Hg in the Cape Fear River Estuary.

5. Quantify the sources and sinks of dissolved Hg, particulate Hg and MeHg in the Cape Fear River Estuary.

Chapter 2 – Methodology

Trace Metal Cleaning Protocols

All Teflon® bottles, vials and distillation apparatus were cleaned using the following protocols. New bottles were processed using a four week cleaning protocol consisting of the following steps: one week soak in 2% Citranox, one week soak in 3 M reagent grade HNO_3, one week soak in 2 M reagent grade HCl and a final week soak in pH 2 (trace metal grade HCl). Bottles and vials were rinsed in between each step three times with deionized (DI) water. After the final step and rinse with DI water, bottles rinsed three times with Milli-Q (MQ) (ultra-pure (>18 MΩ) water produced by a Plus Ultra-pure water system (Millipore, Bedford, MA) and were stored containing 10% trace metal grade HCl and double bagged to prevent contamination. Vials and distillation apparatus were double bagged to prevent contamination. After the initial cleaning protocol was completed, dirty bottles, vials and distillation apparatus were cleaned by an overnight soak with 2% Citranox and an overnight soak in hot reagent grade concentrated HNO_3. Glassware used for reagents and ethylation of MeHg were cleaned by soaking overnight in 10% reagent grade HNO_3, rinsed three times with DI water, rinsed three times with MQ water and then stored in 10% trace metal grade HCl. All bottles and glassware stored in 10% HCl were rinsed three times with Milli-Q before use for sample collection or reagent preparation.

Total Hg Reagents and Standards

Reagents used for Hg analysis were trace metal grade materials from VWR, J.T. Baker, Aldrich Chemical, or Fisher Scientific, unless otherwise noted. All solutions were

prepared using Milli-Q. All reagents were prepared in trace metal clean Teflon® bottles using trace metal clean procedures, unless otherwise noted. Milli-Q water (>18 MΩ) was used for all analyses, reagent and standard preparations. A 0.2 N bromine monochloride solution was prepared in a fume hood by dissolving 11 g reagent grade KBr and 16g reagent grade $KBrO_3$ in 200mL of Milli-Q and shaken to partially dissolve the mixture. 800ml of 12 M T-HCl were carefully added to the mixture. The addition resulted in a color change from yellow to red to orange. The bottle was capped loosely and allowed to vent in the fume hood until cool. The bottle was then capped tightly, double bagged and stored in the dark at room temperature. A 3% stannous chloride solution was prepared daily by dissolving, 30 g of $SnCl_2 \cdot 2H_2O$ in 10 mL 12 M trace metal grade HCl and diluting to 1.0 L with Milli-Q. A 3 % hydroxylamine hydrochloride solution was prepared by dissolving 75 g of $NH_2OH \cdot HCl$ in Milli-Q and bringing the volume to 250 mL. This solution was purified by addition of 125 μL $SnCl_2$ solution and purging overnight at 500 mL min^{-1} with Hg-free N_2 to remove Hg. The stock Hg standard, (Fluka) contained 4.99 mM Hg as $Hg(NO_3)_2 \cdot H_2O$ and was stable for one year or until the expiration date (EPA, 1995). The secondary Hg standard (4.99 μM) was a dilution of 100 μL of the stock Hg standard with 500 μL BrCl solution diluted to 100 g gravimetrically in a Teflon bottle with Milli-Q. Working Hg standards A, 49.9 nM, and B, 0.499 nM, were prepared monthly by gravimetrically diluting 1.0mL and 10 μL of the secondary Hg standard, respectively, with 500 μL BrCl and 100 g Milli-Q.

The calibration curve for total Hg was made using both working standards. Calibration blanks were made gravimetrically using 50 g of Milli-Q and adding 250 μL BrCl in sterile centrifuge tubes and 75 μL NH_2OH before analysis. All calibration standards were made by adding serial dilutions of either working standard to a final volume 50mL of Milli-Q

containing 250 µL BrCl. The first set of standards were prepared by sequential addition of 100, 250 µL, and 1.0 mL of working standard B producing concentrations of 1.0, 2.5, and 10 pM. The second set of standards was prepared by addition of 25, 75 and 125 µL of working standard A to produce concentrations of 25, 75, and 125 pM. The bottles containing the standards were capped and inverted to mix the solutions and allowed to react for a minimum of 30 minutes. Finally, 75 µL of NH_2OH was added to each bottle and mixed until the excess BrCl was destroyed and the yellow color disappeared.

MeHg Reagents and Standards

Reagents used for Hg analysis were trace metal grade materials from VWR, J.T. Baker, Aldrich Chemical, or Fisher Scientific, unless otherwise noted. A 1% ammonium pyrrolidine dithiocarbamate (APDC) solution was prepared by dissolving 1.0 g of reagent grade APDC in 100 mL of Milli-Q. A 0.2 M acetate buffer was prepared by dissolving 136 g of reagent grade sodium acetate in 59 mL of glacial acetic acid and diluting to 500 mL with Milli-Q. The buffer was purified by adding 250 µL of 1% sodium tetraethylborate (ethylating agent) and then purged with UHP Ar overnight to remove traces of MeHg. A 1% sodium tetraethylborate ($NaBEt_4$) solution was prepared by adding 5 mL of 0^oC 2% KOH to a 1.0 g bottle of $NaBEt_4$. The solution was then shaken to dissolve the $NaBEt_4$, and then poured into a 100 mL fluoropolymer bottle containing 95 mL of 0^oC 2% KOH and shaken. Immediately the 1% $NaBEt_4$ solution in 2 % KOH was poured into fifteen 7 mL fluoropolymer bottles that were capped and stored in a low temperature freezer. Before use, a bottle was removed and thawed until a liquid layer formed. The reagent was then used until just before all the ice had melted. This reagent was usually good for one day of running if placed in the refrigerator between uses. Frozen bottles of $NaBEt_4$ of will keep for at least one

week. NaBEt$_4$ is toxic, gives off toxic gases (triethylboron), and is spontaneously combustible. It is imperative that this reagent be exposed to air a minimum length of time. (EPA, 2001b). Unused NaBEt$_4$ was discarded into a large beaker of 1 N HCl in a fume hood. The triethylboron then bubbled off. The acid in the beaker was left in the fume hood until it was boiled down to half volume to destroy residues before discarding as acid waste.

The stock MeHg standard, (Alfa Aesar) contained 1ppm (3.98 μM) MeHg as CH$_3$HgCl. This had an indefinite lifetime when stored in amber glass bottle with a fluoropolymer lid at room temperature (EPA, 2001b). A secondary MeHg stock (20 nM) was prepared by diluting 503 μL of stock MeHg solution to 100 g of Milli-Q containing 500 μL concentrated glacial acetic acid and 200 μL concentrated HCl. The secondary MeHg solution is stable for over a year when stored in a fluoropolymer bottle in the refrigerator (EPA, 2001b).   A working MeHg standard (0.5 nM) was prepared by diluting 2.51 mL of stock MeHg solution to 100 g of Milli-Q containing 500μL concentrated glacial acetic acid and 200 μL concentrated HCl. This solution is stable for more than one month when kept in a fluoropolymer bottle at room temperature.

The calibration curve for MeHg analysis was prepared using the working MeHg standard in the range of 0.1 to 1.0 pM. Each standard was prepared using 50 mL of Milli-Q water, an aliquot 10, 20, 40, 60, or 100 μL of the working MeHg standard, 300 μL of acetate buffer and 40 μL of NaBEt$_4$. The calibration blank was prepared using 50 mL of Milli-Q water, 300 μL of acetate buffer and 40 μL of NaBEt$_4$.

Analysis of Total Hg

Total (THg) and dissolved (TDHg) Hg samples were analyzed following the procedures in EPA method 1631. Total Hg (THg) is defined as all BrCl-oxidizable Hg

species found in an unfiltered aqueous solution. This includes, Hg(II), Hg^o, organo-complexed Hg(II) compounds, particulate Hg, and some covalently bound organo-mercurials (EPA, 1995). BrCl has been found to be an excellent oxidant and preservative for total Hg (Szakacss et al., 1980). This oxidant has been shown to be ideal because it is as effective as hot oxidation and contamination free (Bloom and Crecelius, 1983). Complete oxidation of organo-mercurials has been shown to take place in minutes (Szakacss et al., 1980). 100 mL samples were preserved by the addition of 1.0 mL BrCl to each bottle until a permanent yellow color was obtained. This color indicates that complete oxidation has occurred. Prior to analysis the preserved sample was reduced with the addition of NH$_2$OH·HCl, at approximately 30% of the volume of BrCl, in order to destroy all remaining BrCl. The volumes of BrCl used to preserve Cape Fear Estuary water and corresponding volumes of NH$_2$OH·HCl are given in Table 2.1. Samples were then reduced by stannous chloride (SnCl$_2$) to produce Hg^o and analyzed using the Tekran 2600 cold vapor atomic fluorescence spectrophotometer and model 2620 autosampler. Unfiltered samples were analyzed for total Hg and water filtered through a 0.2 μm cartridge filter were analyzed for total dissolved Hg with particulate Hg found by difference. A calibration curve with standards ranging from 0 pM to 125 pM was constructed prior to sample analysis.

Analysis of MeHg

Total (TMeHg) and dissolved MeHg (MeHg) samples were collected and analyzed using procedures from EPA method 1630 (EPA, 2001b) with Brooks Rand and Tekran instrumentation. Samples were preserved using 9M trace metal grade H$_2$SO$_4$ for saline samples and 12M trace metal grade HCl for freshwater samples. Distillation of MeHg from solution requires a carefully controlled level of HCl in solution. Distillation will not be

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Table 2.1. Volumes of BrCl used to preserve Cape Fear Estuary water for the analysis of total Hg and volumes of NH_2OH used to destroy excess BrCl in each sample.

Sample Size	Volume of BrCl to be added	Volume of NH₂OH to be added
1 L	5 mL	1.5 mL
500 mL	2.5 mL	750 μL
250 mL	1.25 mL	375 μL
100 mL	500 μL	150 μL
50 mL	250 μL	75 μL
30 mL	150 μL	45 μL

quantitative if too little HCl is added, but too much HCl results in co-distillation of HCl

fumes, which interfere with the ethylation procedure. Therefore fresh water samples must be

preserved only with between 0.3% and 0.5% (v/v) (EPA, 2001b). Sampling blanks

consisting of Milli-Q were taken for all samples. The volumes of H_2SO_4 and HCl used to

preserve Cape Fear Estuary water are given in Table 2.2.

In accordance with USEPA Method 1630 water samples were distilled at 125 ± 3^0C

and the distillate collected. Four heating blocks accommodating three distillation vials each

were placed in a frying skillet and brought to a temperature of 125 ± 3^0C. 45 mL aliquots of

samples were poured into pre-weighed distillation vials and exact masses recorded. 200 uL

of 1 % APDC solution was added to vials to prevent the co-distillation of inorganic Hg and

distillation caps were securely fastened. 5 mL of Milli-Q was added to receiving vials

engraved with a 40mL mark and caps were securely fastened. Distillation vials were placed

in heating block and connected to receiving vials with an argon gas flow of 60 ± 20 mL/min.

Receiving vials were held in a Styrofoam cooler filled with ice. Samples were distilled until

each of the twelve receiving vials was filled to the engraved 40 mL line leaving behind 5 mL.

Upon distillation to 40 mL, Teflon tubing on the receiving vials was looped around to close

off the second port of the cap and samples stored at room temperature until analysis no

longer than 48 hours later.

Immediately before analysis, 10 mL of Milli-Q was added to each distillate vial and

then poured into a glass reaction vessel/bubbler. 500 μL of 2 M acetate buffer and 40 μL of

freshly thawed NaBEt4 was added to bubbler, swirled and allowed to react for 17 minutes to

convert all MeHg to volatile methylethylHg. After reaction, a graphitic carbon Carbotrap[®]

was attached to each bubbler with a fluoropolymer fitting. The sample was then purged with

Table 2.2. Volumes of 9M H_2SO_4 and 12M HCl used to preserve Cape Fear Estuary water for the analysis of MeHg.

Saline Samples		Freshwater Samples	
Sample Size	Volume of H_2SO_4	Sample Size	Volume of HCl
1 L	2 mL	1 L	4 mL
500 mL	1 mL	500 mL	2 mL
250 mL	500 μL	250 mL	1 mL
100 mL	200 μL	100 mL	400 μL
50 mL	100 μL	50 mL	200 μL
30 mL	60 μL	30 mL	120 μL

argon for 17 minutes at 200 mL/min.   Absorbed water was removed in the Carbotrap® by connecting the argon line directly to the trap and allowing it to dry for 7 minutes. According to USEPA Method 1630 dried traps are stable for up to 6 hours.

Samples were analyzed by connecting Carbotraps® to the GC column using a fluoropolymer fitting. A nichrome wire coil was placed around the Carbotrap®, centered over, and extending beyond, the packing material. Argon gas line with flow rate of 40 mL min^{-1} was connected to the other end of Carbotrap® and gas was allowed to flow for 30 seconds. The sample was then thermally desorbed from trap by heating of the nichrome wire for 45 seconds. The desorbed methylethylHg was carried through a pyrolytic decomposition column, which converts organo-Hg forms to elemental Hg^o, and then into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection (USEPA Method 1630). Calibration blanks consisting of 50 mL of Milli-Q water, 300 μL of sodium acetate buffer and 40 μL of NaBEt$_4$ were analyzed following the above steps for purging and sample analysis.   Unfiltered water samples were analyzed for TMeHg, water samples filtered through a 0.2 μm cartridge filter were analyzed for dissolved MeHg and particulate MeHg (MeHg$_{part}$) was found by difference.

Quality Analysis and Quality Control

Quality control for the analysis of total Hg and MeHg was conducted by initial demonstration of laboratory capability to establish method detection limit, generate acceptable initial precision and recovery (IPR) and assess performance by analyses of matrix spikes (MS) and matrix spike duplicates (MSD). The aqueous total dissolved Hg detection limit was 0.5 pM (3 times standard deviation of blank). Percent recovery of IPR solutions for TDHg was 97%, with relative standard deviation (RSD) of 2%. The acceptance criteria for

IPR solutions based on Method 1631 are 79 – 121% recovery and 21% RSD. Average recovery of MS and MSD solutions for TDHg was 100%, and relative standard deviation was 12%. The acceptance criteria for MS and MSD solutions based on Method 1631 are 71 – 125% recovery and 24% RSD. Percent recoveries for IPR, MS and MSD fall within the ranges set by Method 1631.

The detection limit for MeHg in aqueous samples was 0.06pM, based on 3 times the standard deviation of blank analysis. Percent recovery of IPR solutions for MeHg was 119%, with relative standard deviation of 13%. The acceptance criteria for IPR solutions based on Method 1630 are 69 – 131 % recovery and 31% RSD. Average recovery of MS and MSD for MeHg was 93%, while relative standard deviation was 17%. The acceptance criteria for MS and MSD solutions based on Method 1630 are 65 – 135% recovery and 35% RSD. Percent recoveries for IPR, MS and MSD fall within the ranges set by Method 1630.

Dissolved Organic Carbon Analysis

Dissolved organic carbon (DOC) was determined by high temperature combustion (HTC) using a Shimadzu TOC 5000 total organic carbon analyzer equipped with an ASI 5000 autosampler (Shimadzu, Kyoto, Japan). Standards were prepared from reagent grade potassium hydrogen phthalate (KHP) in Milli-Q Plus deionized water. Samples and standards were acidified to pH 2 with 2 M reagent grade HCl and sparged with CO_2-free carrier gas for 5 min at a flow rate of 125 ml min^{-1} to remove inorganic carbon prior to injection onto a heated catalyst bed (0.5% Pt on alumina support, 680°C, regular sensitivity). A non-dispersive infrared detector measured CO_2 gas from the combusted carbon. Each sample was injected 4 times. The relative standard deviation was < 3%. The detection limit for this instrument is 5 μM. All samples were run in triplicate.

Chapter 3 – Distribution of Hg in the Cape Fear River Estuary

INTRODUCTION

The determination of Hg concentrations, speciation and distributions in estuarine

environments is the first step in elucidating the fate of Hg in estuaries. Once Hg enters

coastal waters, whether by natural or anthropogenic sources, it may undergo a variety of

chemical transformations and be affected by numerous estuarine processes. Hg^{2+} delivered

to coastal systems can be reduced to Hg^o, with potential evasion to the atmosphere,

methylated, scavenged and buried in sediments, or removed as water enters the oceans

(Fitzgerald et al., 2007).

A portion of inorganic Hg is converted to MeHg that provides a pathway for

bioaccumulation and increased human exposure. The primary organisms responsible for the

methylation of Hg are sulfate reducing bacteria which inhabit anoxic environments

(Compeau and Bartha, 1985; Choi and Bartha, 1994; Heyes et al., 2006; Whalin et al., 2007).

The conversion of inorganic Hg that results in the transport of Hg away from zones of

methylation will lead to reduced MeHg available for bioaccumulation (Whalin et al., 2007).

A small fraction of Hg transported in rivers is exported to the ocean due to the high

retention of Hg in coastal environments (Mason et al., 1993; Benoit et al., 1998; Mason et al.,

1999; Conaway et al., 2003). Retention of Hg within estuaries provides a source of Hg for

participation in a variety of biogeochemical processes. Even though there is documented

contamination of fish in the Cape Fear River estuary, no research has been done to elucidate

the processes affecting the concentration, speciation and distribution of Hg in this economically important estuary.

Chapter Objective

1.   Determine the concentration, speciation and distribution of Hg in the Cape Fear River Estuary.

METHODS

Estuarine and Riverine Sampling

Sampling Sites

The Cape Fear River Estuary was sampled on eleven cruises between July 2004 and September 2006. Sampling of the estuarine portion of the Cape Fear watershed was conducted on all eleven cruises (Figure 1.1). Station descriptions for both riverine and estuarine stations are found in Tables 3.1 and 3.2. Sampling occurred at eight stations from north to south in the estuary: HB, NAV, M61 (across from a state shipping port, just south of Wilmington), M54, M42, M35, M23 and M18. The average salinity range for these sites is 0 – 32. Sampling of the riverine stations occurred on 5 separate cruises the day after the estuarine sampling took place. The upper sampling regime consisted of four stations in the mainstem Cape Fear River (NC11, AC, DP and IC). An additional station, LVC, lies between NC11 and AC at the mouth of Livingston Creek. This site is important because it lies downstream of the former Holtra Chem Corp. This plant was a chlor-alkali manufacturing facility that utilized the Hg cell process for the production of sodium hydroxide, chlorine gas and bleach. These stations were consistently freshwater, with salinity ≤ 0.1. Station BBT represents the Black River, which is a major tributary to the Cape Fear River. Station NCF6 is in the Northeast Cape Fear River, the other major tributary to the

Table 3.1. Station locations and descriptions for the riverine portion of the Cape Fear River estuary. Data and station descriptions from Lower Cape Fear River Program (Mallin et al., 2007). DWQ number represents the NC Division of Water Quality station designation number.

Station	DWQ Number	Location	Importance
NC11	B8360000	At NC 11 bridge on Cape Fear River (CFR) N 34.39663 W 78.26785	Represents water entering the lower watershed from upstream
LVC	B8445000	40 m up Livingston Creek from Cape Fear River N 34.35180 W 78.20128	Below Wright Chemical Plant
AC	B8450000	5 km downstream from International Paper on CFR N 34.35547 W 78.17942	Below International Paper discharge
DP	B8460000	At Dupont Intake above Black River N 34.33595 W 78.05337	At dissolved oxygen sag from International Paper, above Black River
IC	B9030000	Cluster of dischargers upstream of Indian Cr. on CFR N 34.30207 W 78.01372	Cluster of dischargers
BBT	none	Black River between Thoroughfare and Cape Fear River N 34.35092 W 78.04857	Influenced by Black River and Cape Fear River

Table 3.2. Station locations and descriptions for the estuarine portion of the Cape Fear River estuary. Data and station descriptions from Lower Cape Fear River Program (Mallin et al., 2007). DWQ number represents the NC Division of Water Quality station designation number.

Station	DWQ Number	Location	Importance
NAV	B9050000	Railroad bridge over Cape Fear River at Navassa N 34.25943 W 77.98767	Downstream of Progress Energy steam plant and Leland Ind. Park
HB	B9050100	Cape Fear River at Horseshoe Bend N 34.24372 W 77.96980	Above confluence with Northeast Cape Fear River
BRR	B9790000	Brunswick River near new boat ramp in Belville N 34.22138 W 77.97868	Sturgeon area, Near Belville WWTP
M61	B9750000	Channel Marker 61, downtown at N.C. State Port N 34.19377 W 77.95725	Downstream of confluence of the Cape Fear River and the Northeast Cape Fear River
M54	B7950000	Channel Marker 54, 5 km downstream of Wilmington N 34.13933 W 77.94595	Below Wilmington, middle of estuary
M42	B9845100	Channel Marker 42 near Keg Island N 34.09017 W 77.93355	Upstream of Snow's Cut, middle of estuary
M35	B9850100	Channel Marker 35 near Olde Brunswick Towne N 34.03408 W 77.93943	Adjacent to Snow's Cut
M23	B9910000	Channel Marker 23 near CP&L intake canal N 33.94560 W 77.96958	Near CP&L intake canal area at Snows Marsh
M18	B9921000	Channel Marker 18 near Southport N 33.91297 W 78.01697	Lower end of the estuary
SPD	B9980000	1000 ft W of Southport WWT plant discharge on ICW N 33.91708 W 78.03717	Upstream of Southport WWTP
NCF6	B9670000	Northeast Cape Fear River near GE dock N 34.31710 W 77.95383	Near GE

Cape Fear River. During the estuarine sampling cruises, stations BRR and SPD were also sampled. Station BRR is on the Brunswick River near the Brunswick County wastewater treatment plant discharge. Station SPD lies past the mouth of the river in the Atlantic Intracoastal Waterway near the Southport wastewater treatment plant discharge.

Water column sampling in the estuary was conducted on the R/V *Cape Fear* and in conjunction with the Lower Cape Fear River Program (LCFRP). Sampling of the freshwater Cape Fear River stations was conducted from smaller boats with the LCFRP. All the stations sampled for this research coincide with those of the LCFRP. The LCFRP has been monitoring water quality parameters at these stations in the Cape Fear River watershed since 1995 (Mallin et al., 2007).

Sampling Procedures

Water samples were collected using a trace metal clean peristaltic or pneumatic pumping system. All Hg samples were collected in acid cleaned FEP Teflon® bottles. For dissolved species samples were filtered on board using an in-line trace metal clean 1.0 μm Meissner Vanguard polypropylene microfiber prefilter and 0.2 μm Meissner Stylux polyethersulfone membrane capsule filters. Total (THg) and dissolved (TDHg) Hg samples were preserved by adding bromine monochloride (BrCl) immediately after collection. Samples were then stored for no more than one week at room temperature until analysis. MeHg samples were preserved by either adding 9 M T-H_2SO_4 to saline samples, to avoid interferences with excess Cl⁻ ions during distillation, or 12 M T-HCl to freshwater samples. In samples with high HCl concentrations, irreproducibility was found to be dominated by the interference caused by chloride co-distilling with water (Bloom and von der Geest, 1995).

MeHg samples were stored refrigerated and in the dark until analysis. Analysis of total Hg and MeHg was performed as described in Chapter 2.

Samples for dissolved organic carbon (DOC) analysis were filtered using 0.2 μm Meissner Stylux polyethersulfone membrane capsule filters, and collected in pre-cleaned glass vials, acidified with reagent grade 6M HCl and refrigerated until analysis. Analysis of DOC was conducted as previously described in Chapter 2. Salinity and water temperature data were collected *in situ* using an YSI 85 temperature/conductivity probe. Total suspended solids (TSS) were also determined by filtering a known amount of water through preweighed, precombusted Whatman GF/F glass filters (0.7 μm) and rinsed briefly with Milli-Q water to remove salts. At the minimum, triplicate filters were collected per station and individually placed in clean petri dishes, then stored on ice until analysis. Filters were then dried at 60°C for 48 hours and weighed for determination of suspended sediment concentrations.

RESULTS

Surface Waters

Distribution of Dissolved and Particulate Hg

Hg concentrations in estuary surface waters were determined on eleven cruises from July 2004 to September 2006 in the Cape Fear River Estuary (CFRE) (Table 3.3). The sites from NC11 to IC were chosen because they deliver approximately 80% of water to the Cape Fear River Estuary whereas sites downriver encompass the entire salinity regime in the estuary. Dissolved Hg (TDHg) concentrations ranged from <1 to 37 pM and particulate Hg (Hg_{part}) ranged from <1 to 46 pM. Concentrations in the CFRE fall within the range of values for moderately impacted estuarine systems, including some large systems along the U.S. East Coast (Table 3.4).

Table 3.3. Average Hg concentrations and standard errors for surface waters of the Cape Fear River Estuary sampled on eleven cruises from June 2004 to September 2006. $MeHg_{part}$ was only measured on two cruises. NA = not analyzed.

Station	n	Salinity	Hg_{part} (pM)	TDHg (pM)	MeHg (pM)	$MeHg_{part}$ (pM)	DOC (μM)	TSS (mg/L)	chl a (μg/L)
NC11	5	0.1	14 ± 4	7 ± 1	0.4 ± 0.1	NA	483	15	3.8
LVC	3	0.1	11 ± 6	10 ± 2	0.7 ± 0.2	NA	610	6	2.3
AC	5	0.1	13 ± 5	7 ± 3	0.4 ± 0.1	NA	863	14	2.7
DP	5	0.1	14 ± 5	5 ± 2	0.3 ± 0.1	NA	706	19	3.0
IC	5	0.1	9 ± 7	7 ± 2	0.6 ± 0.2	NA	835	12	1.7
NAV	5	0.2	22 ± 7	8 ± 2	0.4 ± 0.1	NA	836	30	2.4
HB	11	0.4	15 ± 2	13 ± 3	0.5 ± 0.2	0.7 ± 0.1	1040	19	4.1
M61	11	3.4	13 ± 2	9 ± 2	0.7 ± 0.3	0.7 ± 0.3	1060	15	4.8
M54	11	5.2	14 ± 3	8 ± 2	0.4 ± 0.1	0.04 ± 0.04	976	19	4.8
M42	10	7.9	6 ± 1	8 ± 2	0.2 ± 0.1	0.5 ± 0.2	914	15	6.5
M35	9	10.7	5 ± 1	8 ± 2	0.2 ± 0.1	2.0 ± 1.6	802	12	7.9
M23	11	19.7	3 ± 1	3 ± 1	0.3 ± 0.1	0.5 ± 0.1	410	12	6.1
M18	9	24.2	2 ± 2	3 ± 1	0.2 ± 0.1	1.6 ± 0.2	420	17	3.8
BBT	5	0.1	11 ± 2	9 ± 3	0.6 ± 0.3	NA	913	NA	1.4
NCF6	5	0.1	15 ± 3	11 ± 4	0.6 ± 0.2	NA	1430	17	1.3
SPD	5	24.5	5.9 ± 1	3 ± 0.1	0.2 ± 0.1	NA	478	20	8.5
BRR	5	1.2	14 ± 5	8 ± 3	0.2 ± 0.1	NA	706	19	3.0

Table 3.4. Comparison of total dissolved Hg and dissolved MeHg concentrations in the Cape Fear River Estuary from stations NC11 to M18 with other estuarine systems.

Location	TDHg (pM)	MeHg (pM)	Reference
Winyah Bay, SC, USA	2 - 28	0.07 – 6.8	Guentzel & Tsukamoto (2001)
San Francisco Bay, CA, USA	0.4 – 170	0 – 1.6	Conaway et al. (2003)
Ochlockonee River, FL, USA	5 – 30	0.29 – 0.46	Guentzel et al. (1996)
Long Island Sound, NY, USA	1.9 – 19.9	NA	Rolfhus and Fitzgerald (2001)
Patuxent River, MD, USA	1 – 7.5	0.02 – 0.15	Benoit et al. (1998)
Lavaca Bay, TX, USA	7.5 – 15.5	0.12 - 1	Bloom et al. (2003)
Connecticut River, CT, USA	1.2 – 17	0.06 – 0.8	Balcolm et al. (2004)
Cheseapeake Bay, MD, USA	NA	0.025 – 1	Mason et al. (1999)
Cape Fear River, NC, USA	0.5 – 37	<0.05 – 1.6	Present Study

Distribution of Dissolved and Particulate MeHg

Dissolved MeHg (MeHg) concentrations were determined on eleven cruises from July 2004 to September 2006 in the Cape Fear River Estuary (Table 3.3). MeHg concentrations ranged from <0.1 to 1.7 pM which is similar to the concentrations reported in other estuarine systems (Table 3.4). MeHg accounted for 0.3 to 75% of TDHg with an average of 10%. High percentages of MeHg ranging from 63 to 75% were found at three stations where TDHg concentrations were low and MeHg concentrations were high. Particulate MeHg (MeHg$_{part}$) concentrations were measured on two cruises at seven stations in estuary. MeHg$_{part}$ concentrations ranged from 0.05 to 1.6 pM. Particulate MeHg ranged from 9 to 82% of the total MeHg at every sampling location during both cruises. In June 2006, MeHg$_{part}$ was found in greater concentration than dissolved MeHg (MeHg) at six of seven stations. In September 2006, dissolved MeHg was greater than particulate at all stations; however MeHg$_{part}$ was a substantial fraction of the total at each location.

Bottom Waters

Distributions of Dissolved and Particulate Hg

Hg concentrations in bottom waters of the Cape Fear River Estuary were determined on six cruises from April 2005 to September 2006 (Table 3.5), and encompassed the entire salinity gradient. Dissolved Hg concentrations in bottom waters ranged from <1 to 32 pM, while particulate Hg concentrations ranged from <1 to 72 pM.

Distributions of Dissolved and Particulate MeHg

Dissolved MeHg concentration in bottom waters of the Cape Fear River Estuary was determined on six cruises from April 2005 to September 2006 (Table 3.5). MeHg concentrations in bottom waters ranged from 0.1 to 1.8 pM. MeHg$_{part}$ in bottom waters were

Table 3.5. Average Hg concentrations and standard errors for bottom water in the Cape Fear River Estuary sampled on five cruises from April 2005 to September 2006. NA = not analyzed.

Station	n	Salinity	Hg part (pM)	TDHg (pM)	MeHg (pM)	MeHg Part (pM)	DOC (µM)	TSS (mg/L)
HB	6	2.2	21 ± 6	14 ± 4	0.5 ± 0.1	0.5 ± 0.3	1200	21
M61	6	7.5	11 ± 3	9 ± 3	0.6 ± 0.3	0.2 ± 0.1	1050	41
M54	4	8.9	12 ± 8	6 ± 4	0.5 ± 0.4	NA	860	NA
M42	3	15.2	10 ± 10	10 ± 9	0.2 ± 0.03	NA	768	NA
M35	2	18.6	23 ± 0.4	15 ± 0.3	0.05 ± 0	NA	638	NA
M23	4	25.4	38 ± 15	4 ± 3	0.4 ± 0.2	NA	413	NA
M18	3	26.8	52 ± 13	4 ± 3	0.2 ± 0.1	0.2 ± 0.1	254	39

determined in June and September 2006 at three stations (Table 3.5). Concentrations of

MeHg$_{part}$ were found to range from 0.1 to 0.8 pM.

<center>**DISCUSSION**</center>

Distribution of Hg – Surface Waters

Distributions of TDHg and Hg$_{part}$ in the surface waters of the Cape Fear River are

illustrated in Figures 3.1 and 3.2. Concentrations of TDHg and Hg$_{part}$ were correlated with

each other in estuarine surface waters only (Table 3.6) indicating that their sources and sinks

may be related. Concentrations of TDHg are consistent in the freshwater stations with the

exception of elevated concentrations found at LVC, approximately 10 pM relative to a

freshwater background concentration of approximately 5 pM. An important aspect of the

sampling locations studied is that they include sites just above river, directly adjacent to and

just down river from a now abandoned chlor-alkali plant (currently a USEPA hazardous

waste site). At LVC, adjacent to waste lagoons from the plant, TDHg concentrations were

always significantly higher (ca. 50%, t-test, $p<0.005$) in relation to values immediately

upstream from the plant at NC11 (Figure 3.1). This suggests that the site at LVC had a

significant local input from the defunct chlor-alkali plant.

Elevated TDHg concentrations were also observed at HB (Figure 3.1), and may be

due to a variety of factors. Concentrations of Hg$_{part}$ were elevated at NAV (Figure 3.2),

which is the next station upstream from HB. Higher values of Hg$_{part}$ at this upstream station

may be the source of elevated TDHg values at HB. It has been suggested that Hg bound and

trapped to organic carbon and the degradation of the organic carbon releases Hg increasing

TDHg found in the water column (Leermakers et al., 1995). It has also been suggested that

<center>45</center>

Table 3.6. Pearson Correlation results for Cape Fear River Estuary surface waters. Sequence of numbers in each box represents *p* value, r value and n.

	Hg part	MeHg	MeHg$_{part}$	Temp	S	DOC	TSS	chla
TDHg	<0.0001 0.339 100	<0.0002 0.370 93	0.440 0.225 14	0.533 -0.056 100	<0.0001 -0.375 100	<0.0001 0.462 95	0.02 0.261 77	<0.0001 -0.384 100
Hg part		0.04 0.210 93	0.169 -0.390 14	0.876 -0.015 99	<0.0001 -0.505 100	<0.002 0.317 95	<0.0001 .597 77	<0.002 -0.309 100
MeHg			0.739 -0.098 14	0.07 0.185 93	0.003 -0.307 93	<0.001 0.348 88	0.595 -0.065 70	0.003 -0.299 93
MeHg$_{part}$				0.514 -0.190 14	0.406 -0.241 14	0.619 0.146 14	0.056 -0.521 14	0.803 -0.074 14
Temp					0.507 0.0612 100	0.090 0.160 95	0.573 -0.289 92	0.105 0.252 120
S						<0.0001 -0.561 95	0.376 -0.102 77	<0.001 0.317 100
DOC							0.034 0.249 72	<0.004 -0.295 95
TSS								0.119 -0.179 77
chla								

Figure 3.1. Distribution of total dissolved Hg in the surface mainstem Cape Fear River Estuary. Stations NC11 to IC represents the average concentration (pM) for 5 sampling cruises, with the exception of LVC which represents 3 samplings. Stations NAV to M18 represents the average concentration (pM) for 11 sampling cruises. Error bars represent the standard error between each sampling cruise. DOC measurements are averages of 11 sampling cruises for each station, and are shown as filled squares. Salinities are presented as averages for each site.

Figure 3.2. Distribution of particulate Hg in the surface waters of the mainstem Cape Fear River Estuary. Stations NC11 to IC represents the average concentration (pM) for 5sampling cruises, with the exception of LVC which represents 3 samplings. Stations NAV to M18 represents the average concentration (pM) for 11 sampling cruises. Error bars represent the standard error between each sampling cruise. TSS measurements are averages of 11 sampling cruises for each station, and are shown as filled squares. Salinities are presented as averages for each site.
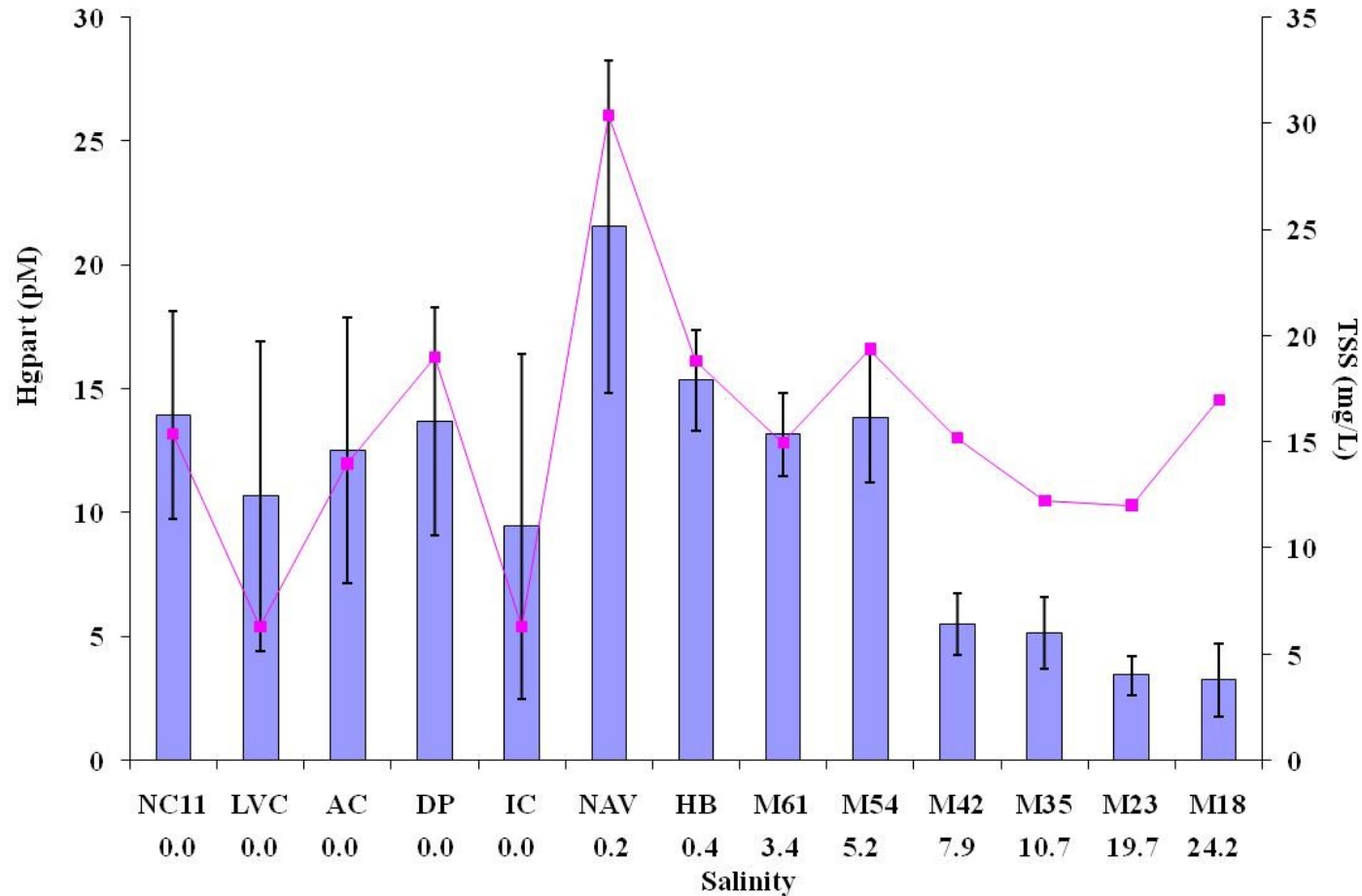
high Hg concentrations associated with suspended particulate matter may lead to an increase in dissolved Hg concentrations (Roth et al., 2001). Particulate Hg at NAV could be degraded influencing the TDHg concentrations at the downstream station.

The concentrations of the various Hg species were examined as a function of river flow to investigate how different flow regimes affect the concentrations and speciation of Hg in the CFRE. Flow rates were calculated using USGS discharge data for the Cape Fear River. Low flow conditions were defined as flow rates <100 m^3 s^{-1}, intermediate flow conditions were between 100 and 300 m^3 s^{-1}, and high flow conditions were >300 m^3 s^{-1}.

TDHg concentrations were higher during mid flow conditions (Figure 3.3). Concentrations were lower when flow in the estuary was high or low, and are dependent on the nature of the sources. TDHg concentrations increased with water discharge in the Loire river and decreased in the Seine River (Coquery et al., 1997), suggesting that the effect of flow is variable between estuaries.

Mixing regimes for TDHg were also analyzed on a cruise by cruise basis for the Cape Fear River. Five of the eleven cruises sampled were conducted under low flow conditions, while three were under intermediate flow and three were during high flow conditions. Under low flow conditions (>100 m^3 s^{-1}), TDHg exhibited conservative mixing in July 2004 and May 2005 (Figure 3.4 a and c), non-conservative mixing on June 2005 and September 2005 (Figure 3.4 d and e) and in August 2004 (Figure 3.4 b) there appears to be addition of TDHg mid estuary. Under intermediate (100 to 300 m^3 s^{-1}) and high flow conditions (>300 m^3 s^{-1}), TDHg exhibits apparent conservative mixing in the estuary (Figures 3.5 and 3.6).

Figure 3.3. Average surface TDHg concentrations (pM) from NC11 to M18 as a function of flow rate (m^3 s^{-1}) at time of sampling. Low flow < 100 m^3 s^{-1}, intermediate flow between 100 and 300 m^3 s^{-1} and high flow > 300 m^3 s^{-1}.
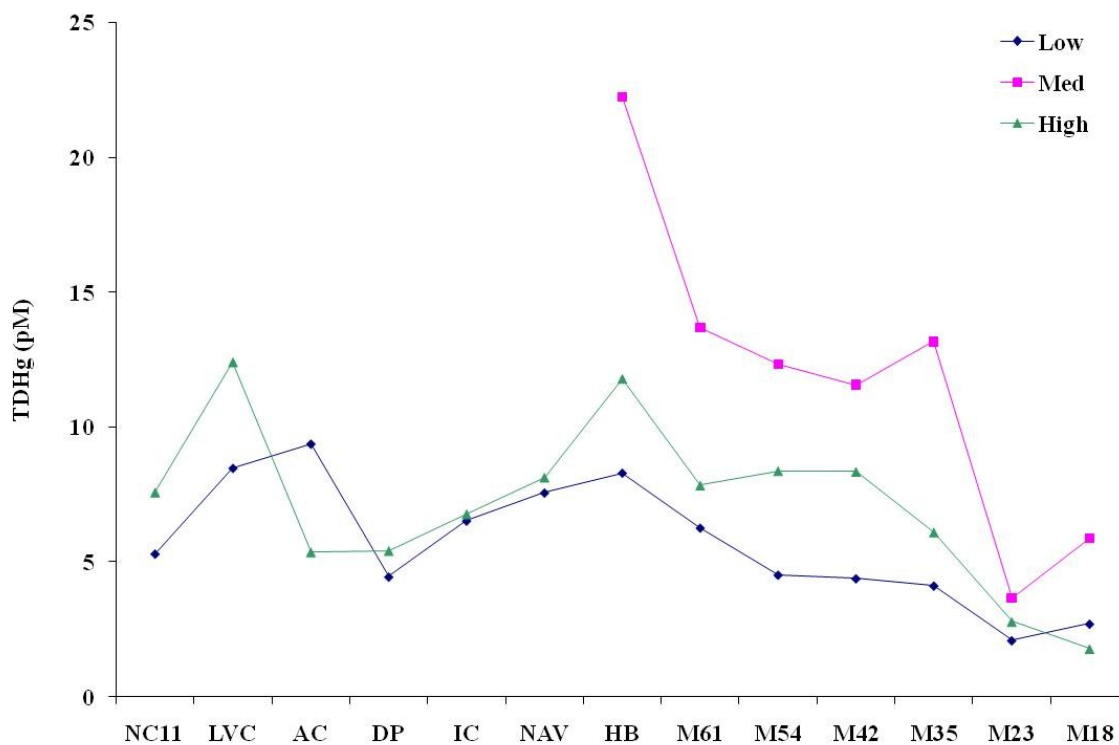
Figure 3.4. Surface water TDHg concentrations (pM) versus salinity for individual cruises during low river flow (< 100 m s^{-1}) regime.

Figure 3.5. Surface water TDHg concentrations (pM) versus salinity for individual cruises during intermediate river flow (100 – 300 m s^{-1}) regime.

Figure 3.6. Surface water TDHg concentrations (pM) versus salinity for individual cruises during high river flow (> 300 m s^{-1}) regime.
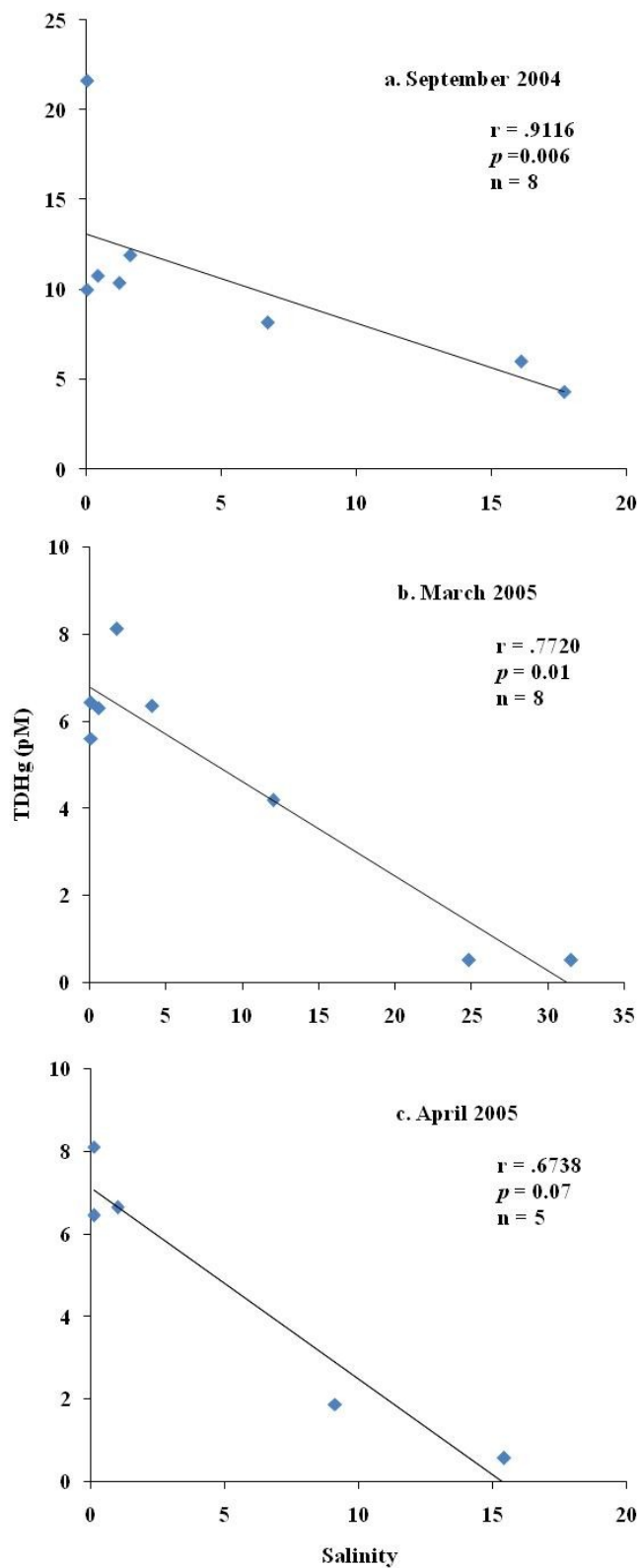
In other estuaries, such as the St. Lawrence, Galveston Bay, Scheldt Estuary and San Francisco Bay, TDHg exhibits non-conservative behavior (Cossa et al., 1988; Leermakers et al., 1995; Stordal et al., 1996; Conaway et al., 2003). These estuaries may be influenced by sources or sinks of Hg that are not found in the Cape Fear River. In the Cape Fear River, medium flow rate influence the concentration of TDHg in the estuary, where concentrations were elevated during t his flow regime with respect to low and high flows. These previous studies have determined mixing behavior based on one to two samplings, w here as the Cape Fear River was sampled eleven times. The increased sampling of the Cape Fear River illustrates the variable mixing regimes of the estuary.

Particulate Hg concentrations are similar to each other in the freshwater stations (Figure 3.2). Elevated concentrations of Hg_{part} and TSS are found at NAV. This station is located near Progress Energy's steam plant and the Leland industrial park and may influence the higher concentrations found at NAV. This also may be an area of geochemical trapping for Hg, and elevated concentrations are a reflection of resuspended particulates in the water column. Concentrations of Hg_{part} are elevated at NAV, possibly due to coal dust or fly ash that may be from two nearby sources, Sutton Steam Plant and WASTEC. The elevated concentrations of Hg_{part} found at NAV decrease moving towards the interface of freshwater and saltwater. TDHg concentrations increase and Hg_{part} decrease at HB, the station downstream of NAV (Figure 3.7). The increase of TDHg and decrease of Hg_{part} could be due to the desorption of Hg from particles found at NAV.

Particulate Hg concentrations were greatest in the freshwater sites during high flow (Figure 3.8). As freshwater was diluted by seawater, particulate Hg returned to lower concentrations that are observed for other flow regimes in the surface waters of the Cape

Figure 3.7. Average concentrations and standard deviations of TDHg and Hg_{part} (pM) at stations near two potential sources of particulate Hg.
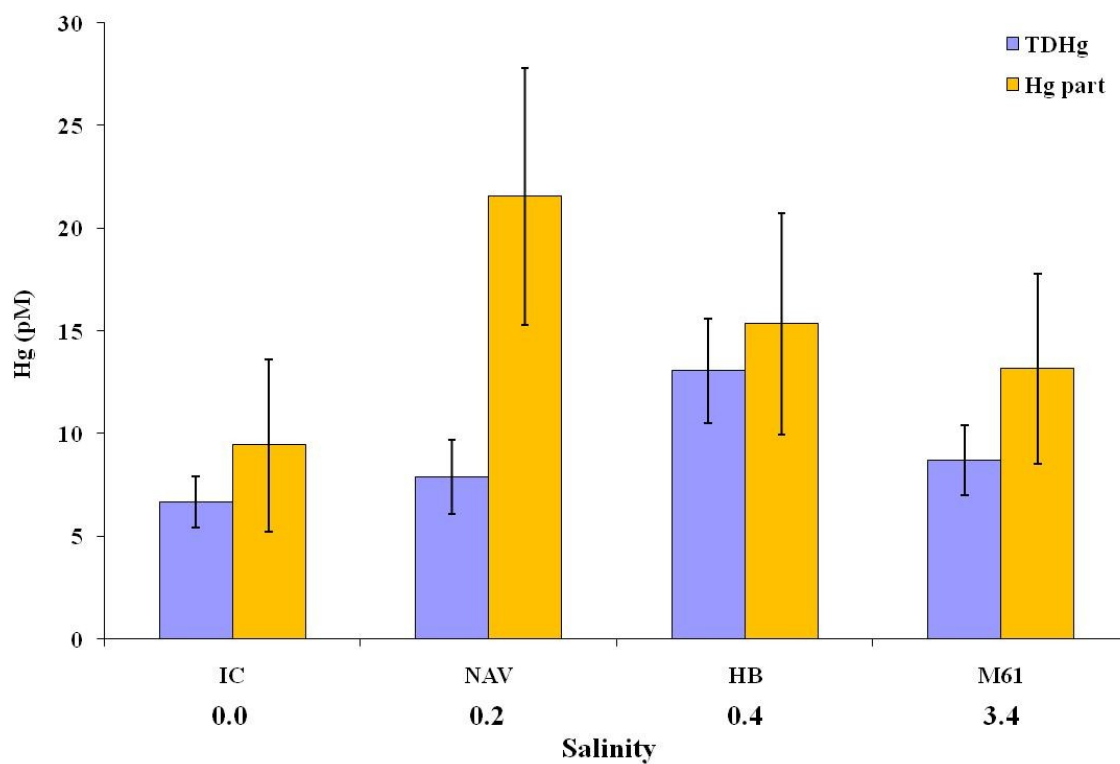
Figure 3.8 Average surface Hg$_{part}$ concentrations (pM) from NC11 to M18 as a function of flow rate (m^3 s^{-1}) at time of sampling. Low flow < 100 m^3 s^{-1}, intermediate flow between 100 and 300 m^3 s^{-1} and high flow > 300 m^3 s^{-1}.
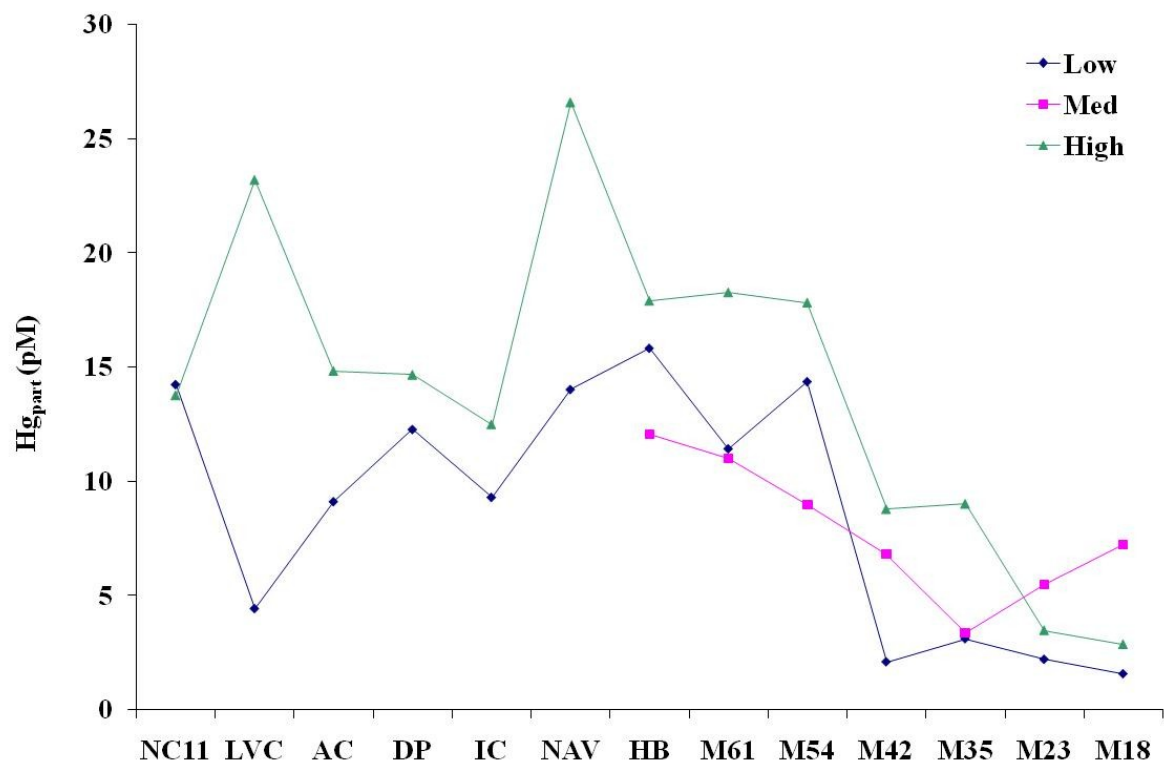
Fear River. This is the same pattern was observed for TSS (Figure 3.9). In the Seine River particulate Hg concentrations were greatest during low river flow, whereas in the Loire River Hg_{part} concentrations increase with increasing water discharge (Coquery et al., 1997). The authors suggest that the variability of particulate Hg concentrations probably results from mixing of particles with varying amounts of Hg. Our data suggest that high flow increases the concentration of particles containing Hg in the freshwater portions of this estuary.   This is also

seen in the tributaries of Chesapeake Bay where high inputs of particles from urban sources and resuspension of sediments during high flow conditions and low residence times were the source of higher Hg concentrations (Lawson et al., 2001a).

Particulate Hg does not exhibit consistent mixing behavior in the Cape Fear River. Under low flow conditions, Hg_{part} appears to be conservatively mixed in March 2004, May 2005 and June 2005 (Figure 3.10 a, c and d) and non-conservatively mixed In August 2004 and September 2005 (Figure 3.10 b and e). Under intermediate flow rates, Hg_{part} shows apparent conservative mixing in June 2006 (Figure 3.11b) and non-conservative mixing with addition at the seawater endmember in February 2006 (Figure 3.11a) and September 2006 (Figure 3.11a). Under high flow rates, there is apparent conservative mixing in March and April 2005 (Figure 3.12 b and c) and non-conservative mixing in September 2004 (Figure 3.12a). The addition of Hg_{part} in the seawater endmembers may be due to biogenic particles found in the more optically clear waters near the mouth of the estuary.

The occasional non-conservative behavior of Hg_{part} has been seen in the St. Lawrence estuary (Cossa et al., 1988), the Scheldt Estuary (Leermakers et al., 1995), Winyah Bay (Guentzel and Tsukamoto, 2001), and Patuxent River Estuary (Benoit et al., 1998). On

Figure 3.9. Average surface TSS concentrations (mg L^{-1}) from NC11 to M18 as a function of flow rate (m^3 s^{-1}) at time of sampling. Low flow < 100 m^3 s^{-1}, intermediate flow between 100 and 300 m^3 s^{-1} and high flow > 300 m^3 s^{-1}.
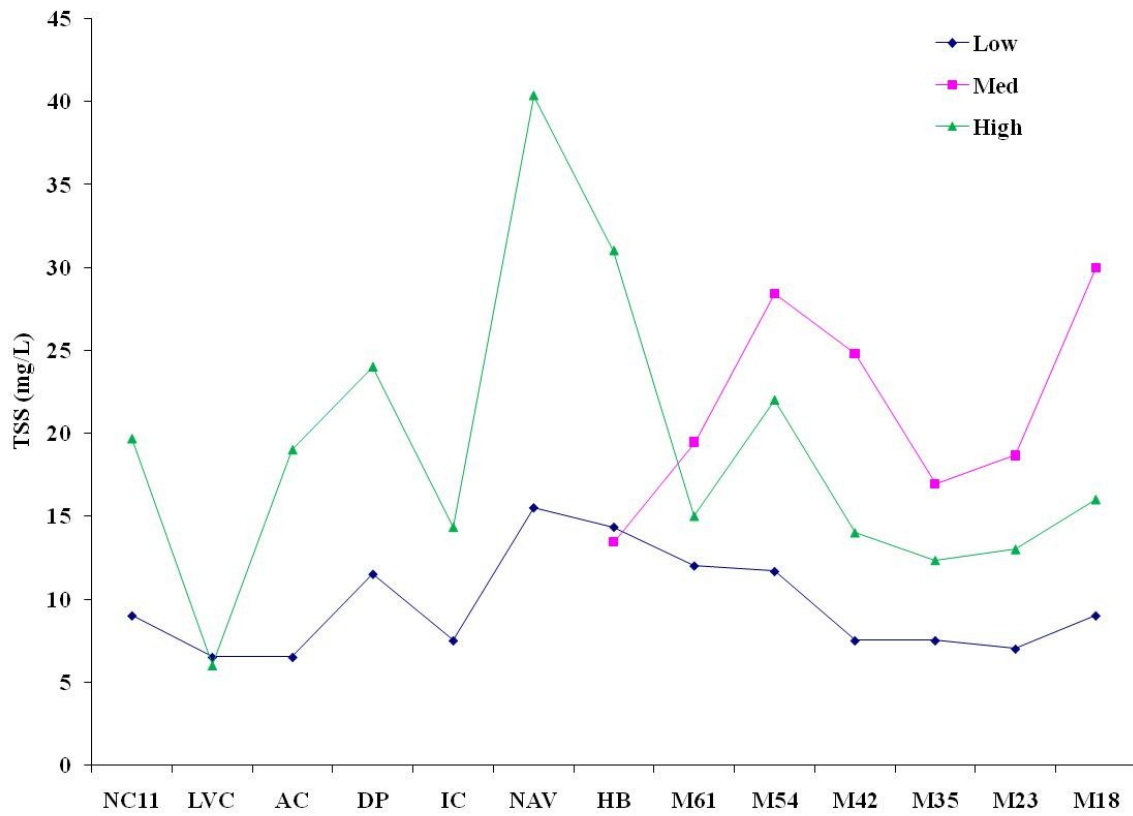
Figure 3.10. Surface water Hg$_{part}$ concentrations (pM) versus salinity for individual cruises during low river flow (< 100 m s^{-1}) regime.
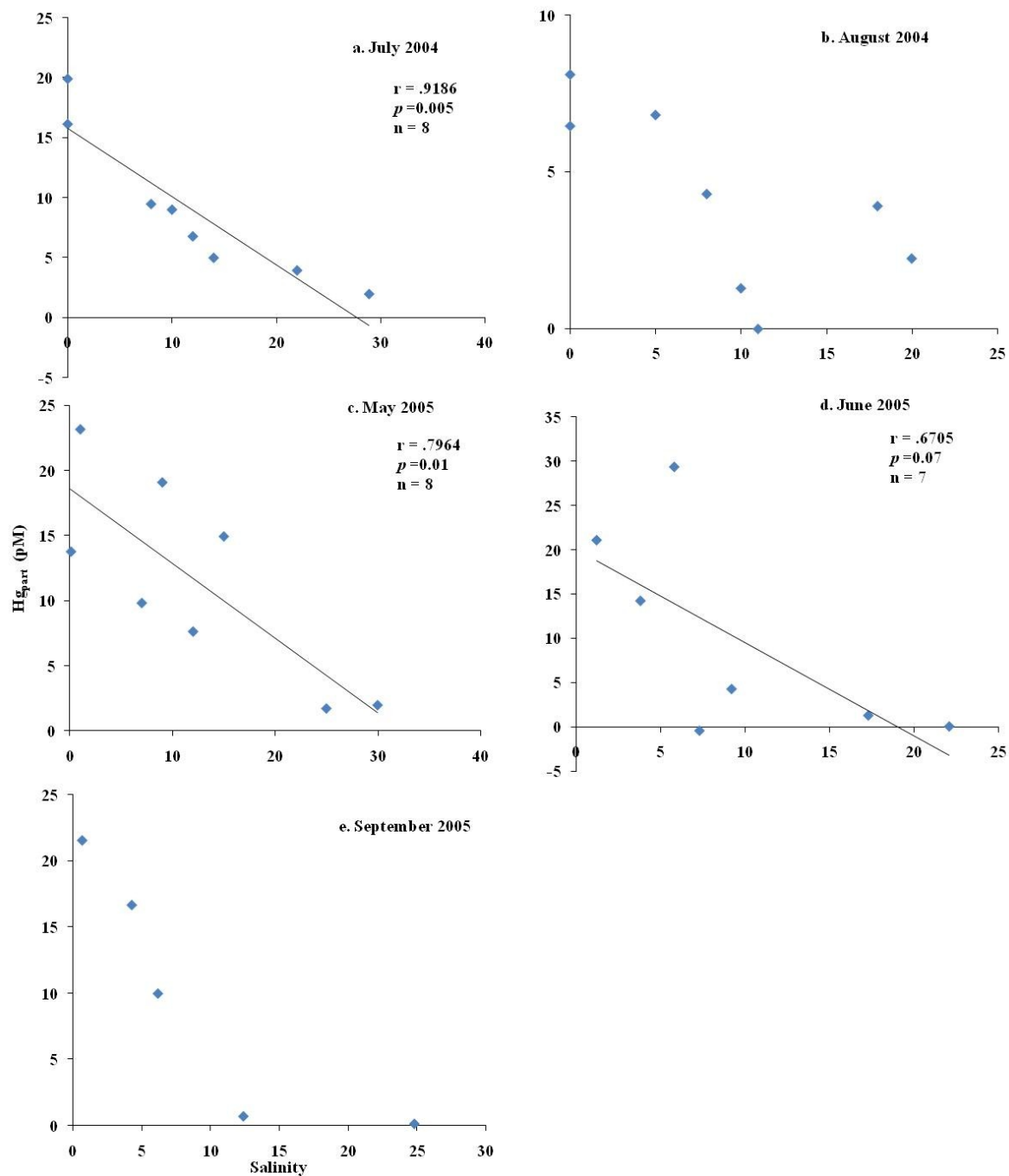
Figure 3.11. Surface water Hg_{part} concentrations (pM) versus salinity for individual cruises during intermediate river flow (100 – 300 m s^{-1}) regime.
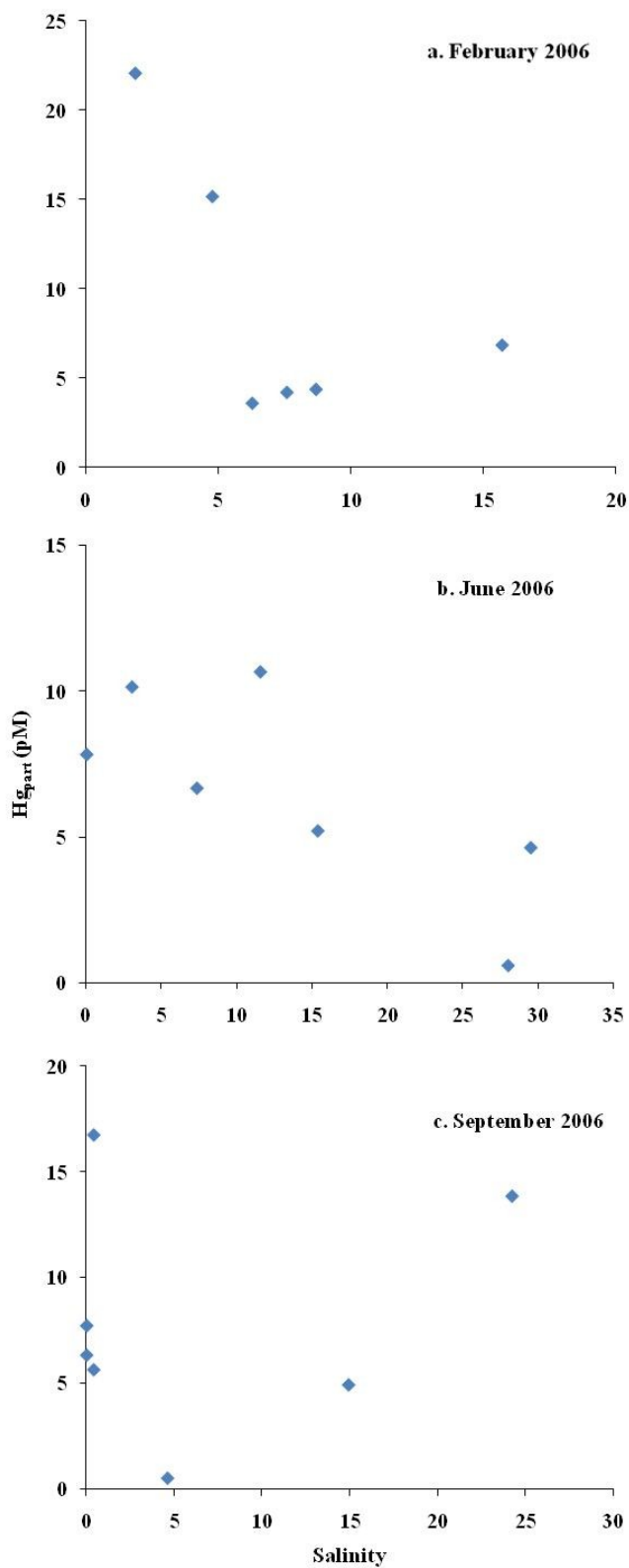
Figure 3.12. Surface water Hg$_{part}$ concentrations (pM) versus salinity for individual cruises during high river flow (> 300 m s^{-1}) regime.
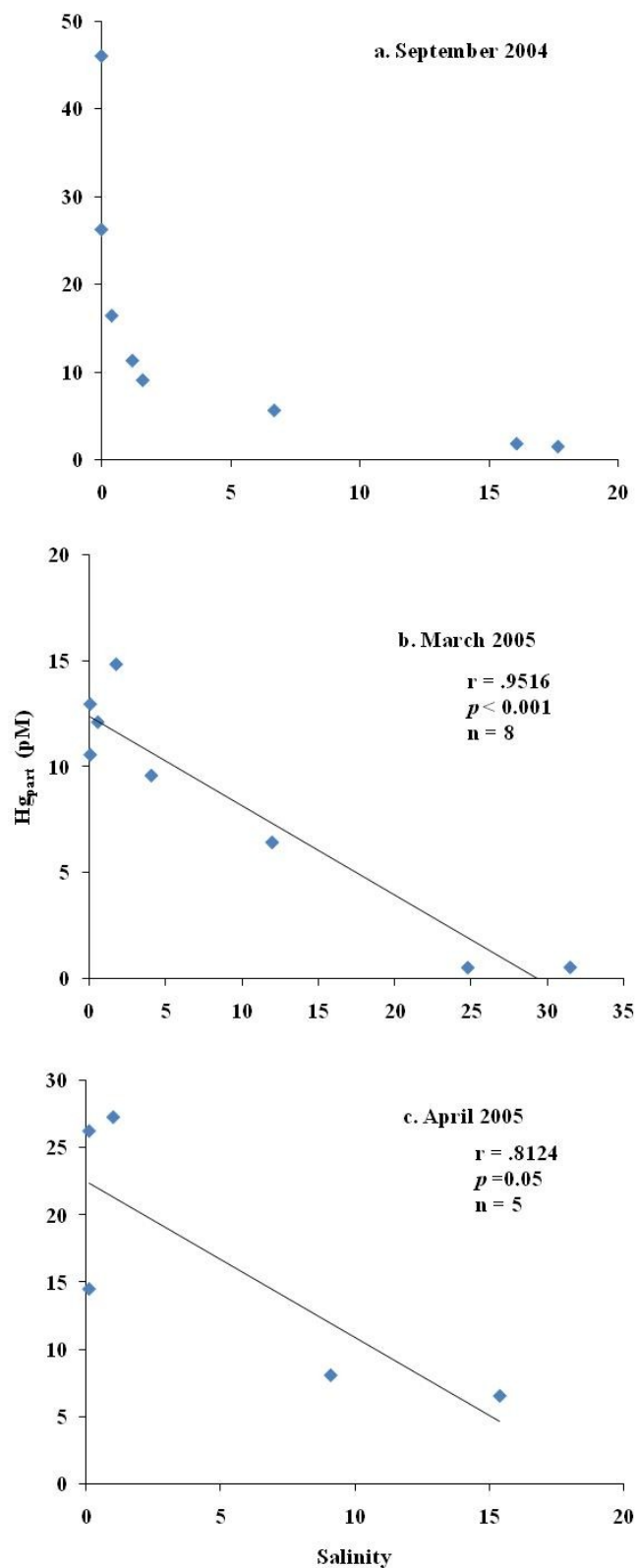
cruises that show non-conservative mixing, maximum removal of Hg_{part} is occurring in the Cape Fear River between salinities of 5 and 11. This removal has also been seen in the Patuxent River (Benoit et al. 1998) and Scheldt Estuary (Leermakers et al., 1995) where a slight decrease is found between salinities of 0 to 5, then a rapid removal occurs from 5 to 20.

Distributions of MeHg and $MeHg_{part}$ in the Cape Fear River are illustrated in Figures 3.13 and 3.14. Concentrations of dissolved MeHg are variable in the freshwater stations, with elevated concentrations (0.6 – 0.7 pM) found at LVC, IC and M61 relative to the remaining sites (0.2 – 0.5 pM). The concentration of MeHg at LVC was not significantly different between these sites suggesting the chlor-alkali plant is a source of TDHg but is not a significant direct source of MeHg. Concentrations of MeHg were correlated with TDHg in surface waters (Table 3.6) which was expected since MeHg is a component of the TDHg found in the estuary. No consistent correlation was found between $MeHg_{part}$ and other ancillary parameters, but it was highly correlated ($p < 0.003$, r = 0.953, n=6) with TDHg in bottom waters.

MeHg concentrations in the Potomac River did not increase with an increase in flow rate (Lawson et al., 2001a). Concentrations of MeHg in the Cape Fear River were highest during periods of high river flow (Figure 3.15). This was also observed in the tributaries of the Chesapeake Bay where concentrations of MeHg are low under base or low flow conditions and increase under conditions of high flow (Lawson et al., 2001a). This increase in MeHg concentrations during high flow may be attributed to runoff originating from surrounding marginal environments such as marshes and wetlands where methylation is enhanced (Lawson et al., 2001a).

Figure 3.13. Distribution of dissolved MeHg in surface waters of the mainstem Cape Fear River Estuary. Stations NC11 to IC represents the average concentration (pM) for 5sampling cruises, with the exception of LVC which represents 3 samplings. Stations NAV to M18 represents the average concentration (pM) for 11 sampling cruises. Error bars represent the standard error between each sampling cruise. Salinities are presented as averages for each site.
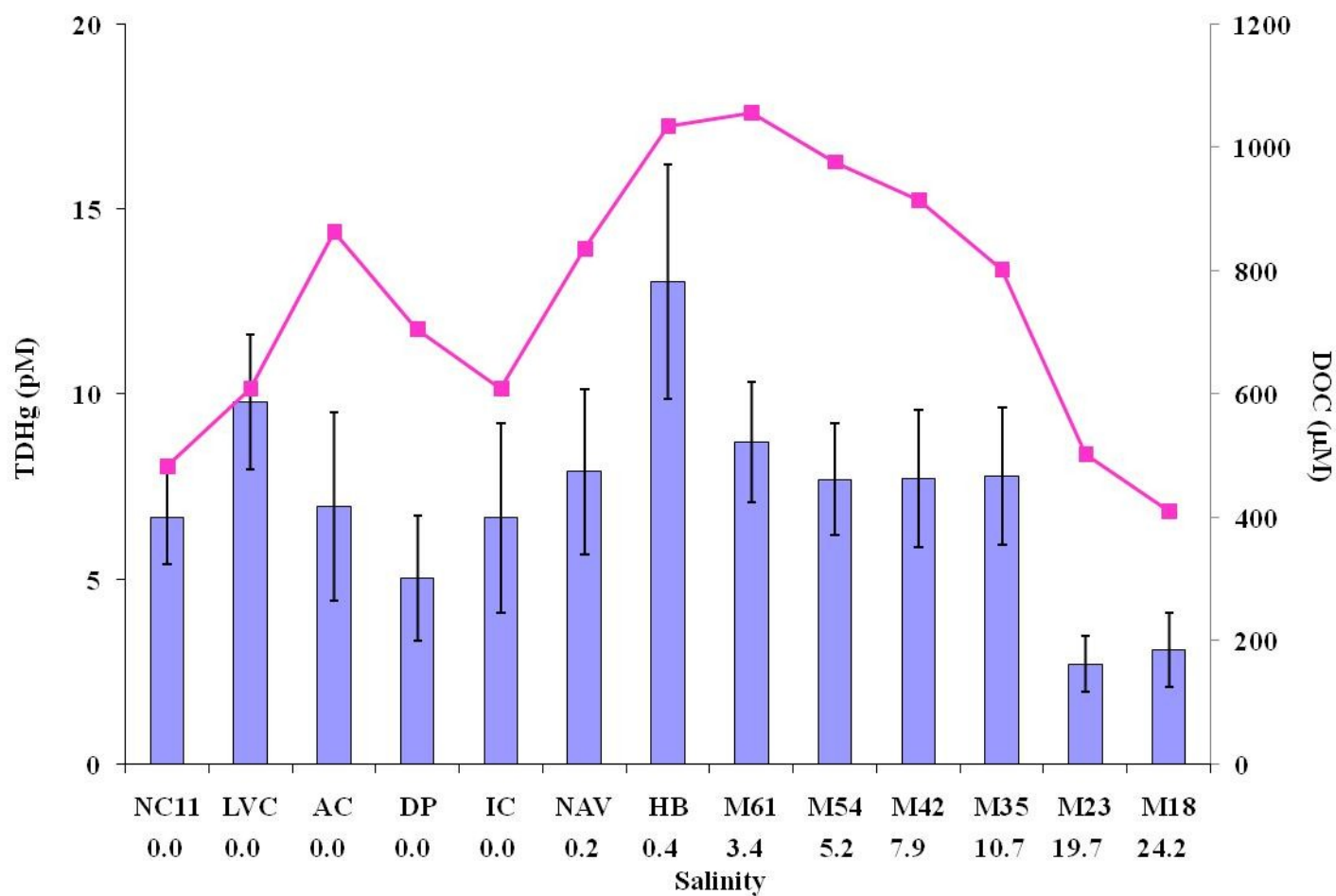
Figure 3.14. Distribution of particulate MeHg in surface waters of the mainstem Cape Fear River Estuary. Each station represents the average concentration (pM) of 2 sampling cruises. Error bars represent the standard error between each sampling cruise.
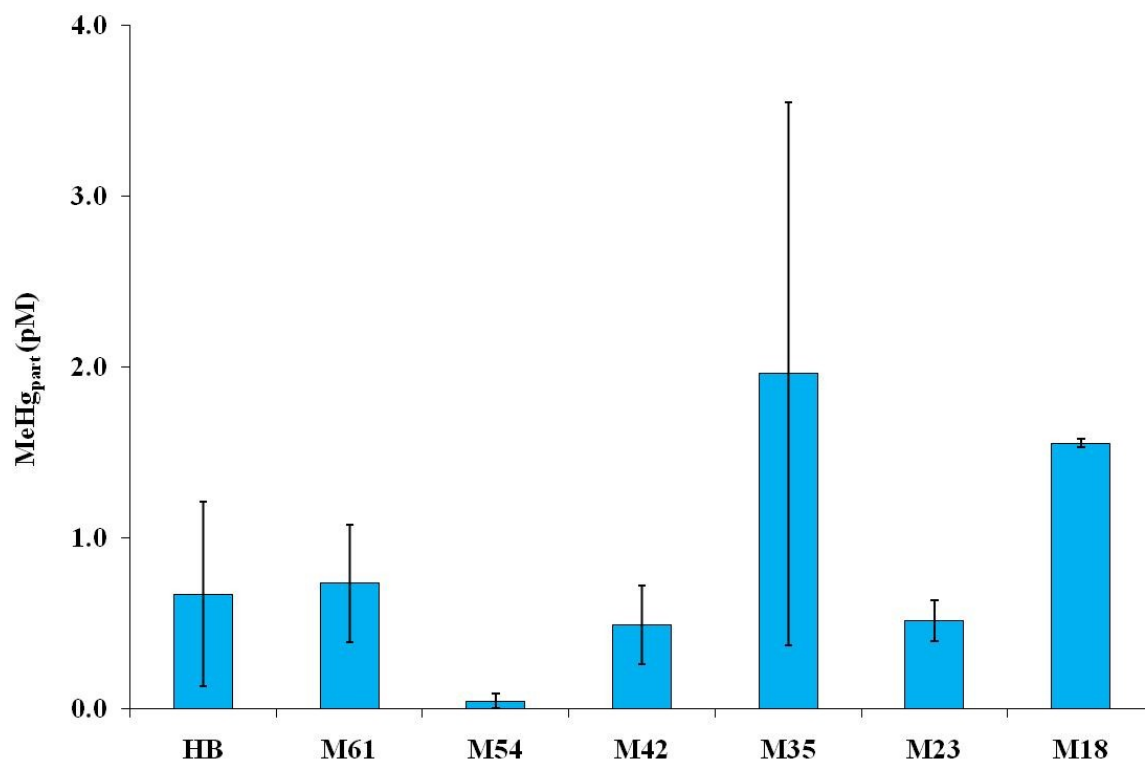
Figure 3.15. Average surface MeHg concentrations (pM) from NC11 to M18 as a function of flow rate (m^3 s^{-1}) at time of sampling. Low flow < 100 m^3 s^{-1}, intermediate flow between 100 and 300 m^3 s^{-1} and high flow > 300 m^3 s^{-1}.
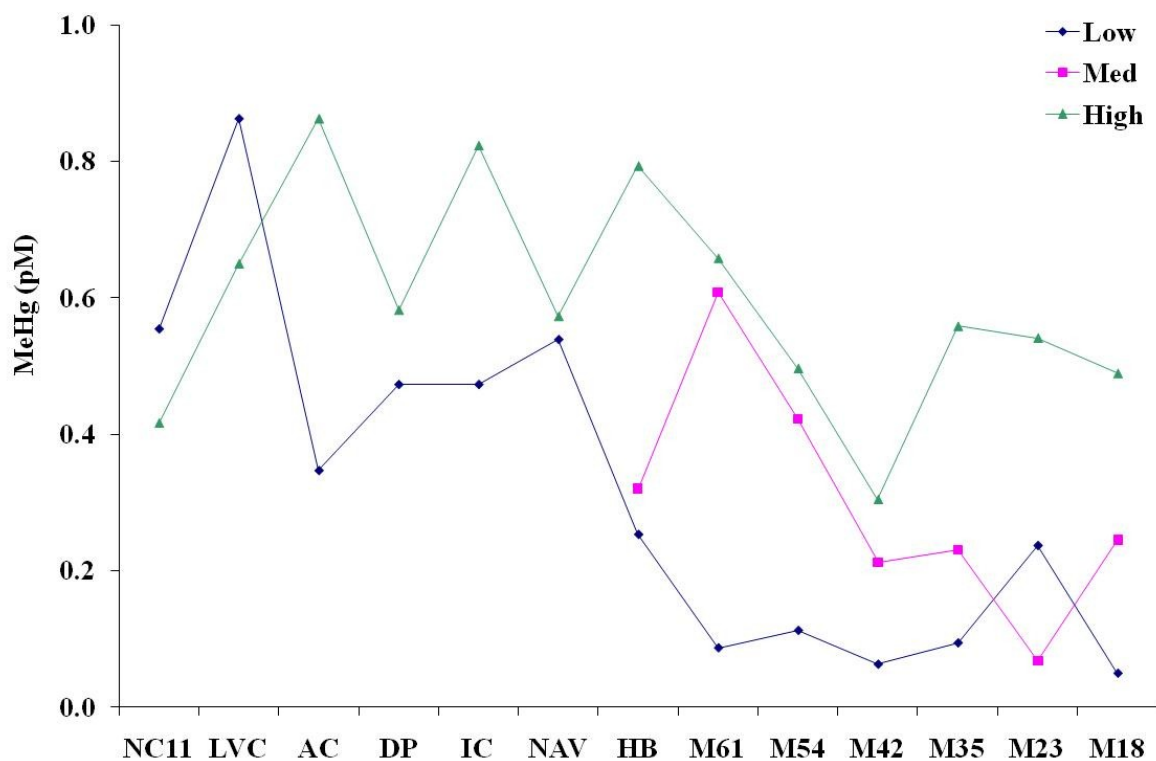
When evaluated by individual cruises, under low flow MeHg concentrations are non-conservatively mixed within the estuary (Figure 3.16). In August 2004, June 2005 and September 2005, there are additions of MeHg throughout the estuary possibly due to biogenic material. Under intermediate flow conditions, MeHg is non-conservatively mixed in the estuary (Figure 3.17). MeHg is non-conservatively mixed under high flow conditions (Figure 3.18). In March 2005, there is addition in the seawater endmember (Figure 3.18b) and in April 2005 there is addition in the mid-estuary.

The Cape Fear River Estuary is a highly turbid, light limited, blackwater, partially mixed estuary. Potential parameters controlling Hg concentrations in this system include salinity, DOC and TSS. TDHg, Hg_{part} and MeHg were all inversely correlated with salinity (Table 3.6), suggesting a riverine source of Hg. The impact of salinity on Hg concentrations can also be seen in Figures 3.1, 3.2 and 3.13 where the average concentration of all Hg species was higher in less saline stations relative to sites downriver such as M35-M18. This distribution of Hg has been documented in other estuaries such as the Patuxent River Estuary (Benoit et al., 1998), Scheldt Estuary (Leermakers et al., 1995), Galveston Bay (Stordal et al., 1996) and the St. Lawrence River (Cossa et al., 1988). It has been suggested that concentrations of Hg are higher in freshwaters because they have not been removed by estuarine processes (Conaway et al., 2003). The low concentrations of the various Hg species found in the saline waters of the Cape Fear River agree with Atlantic Ocean Hg data from Bermuda, where concentrations of dissolved Hg are <2.5 pM and concentrations of MeHg are <0.05 pM (Fitzgerald et al., 2007).

Salinity and DOC were inversely correlated (Figure 3.19) similar to what has been observed in an earlier study in this estuary by Avery et al. (2001). The authors suggest that

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Figure 3.16. Surface water MeHg concentrations (pM) versus salinity for individual cruises during low river flow (< 100 m s^{-1}) regime.
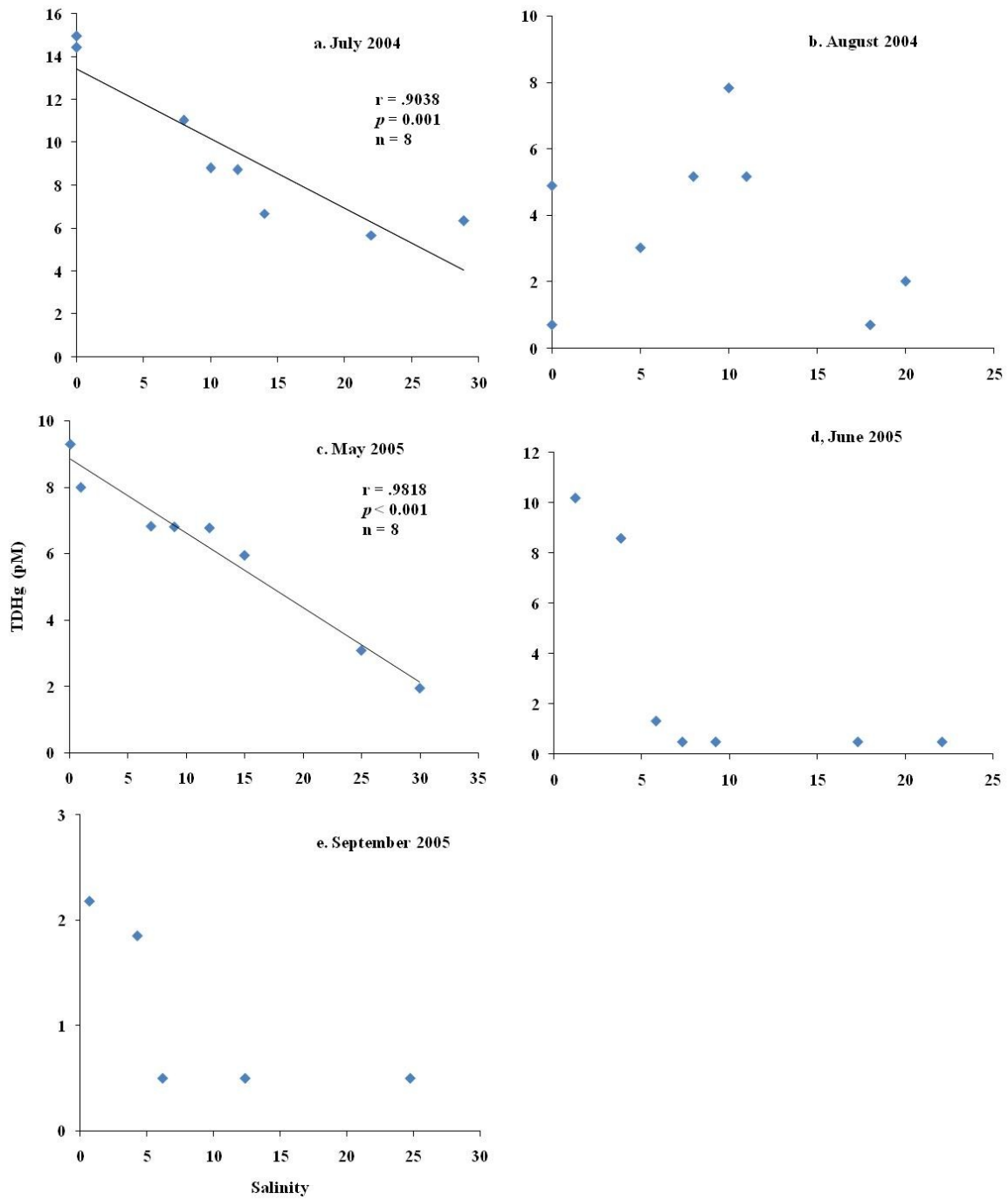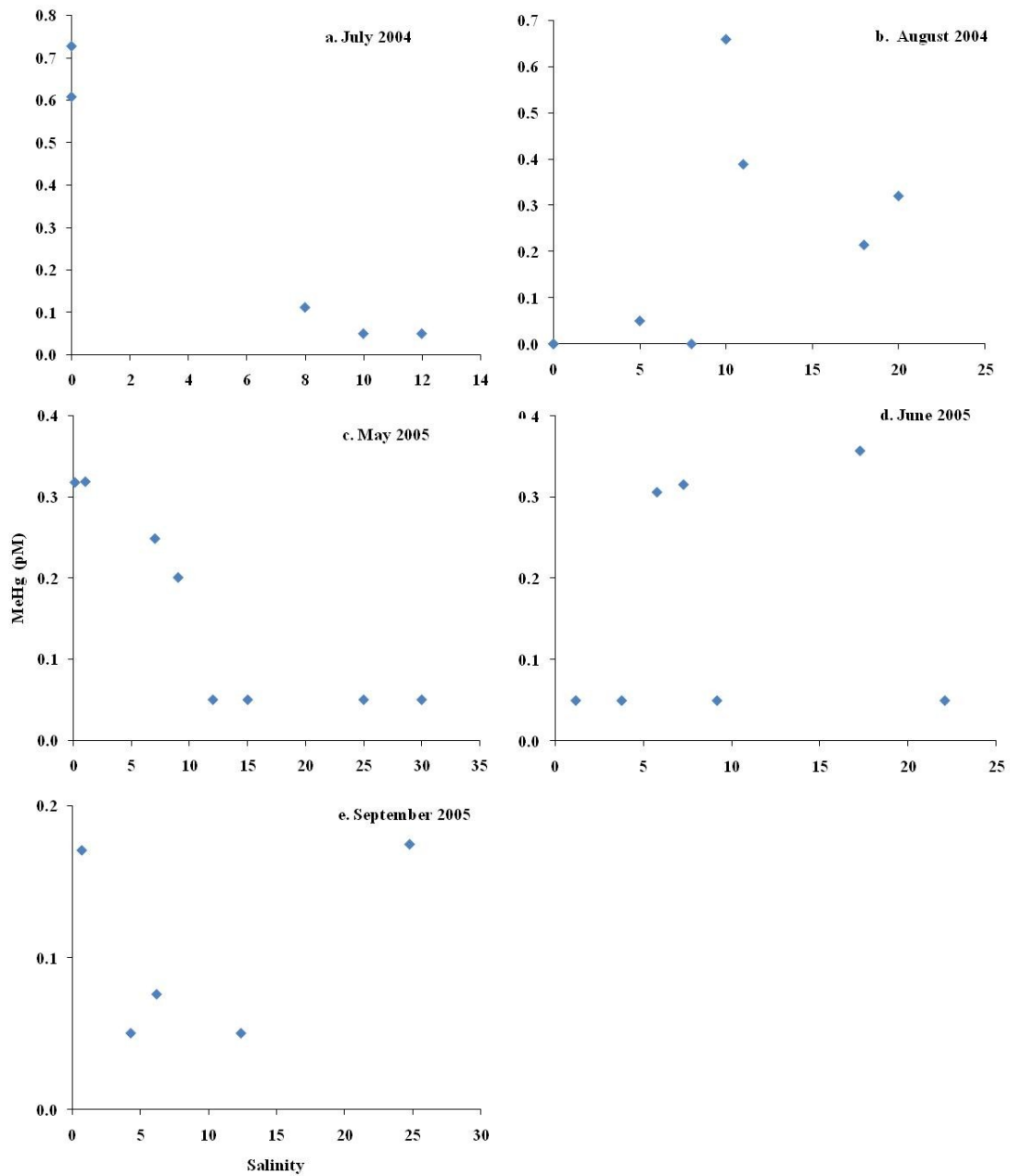
Figure 3.17. Surface water MeHg concentrations (pM) versus salinity for individual cruises during intermediate river flow (100 – 300 m s^{-1}) regime.
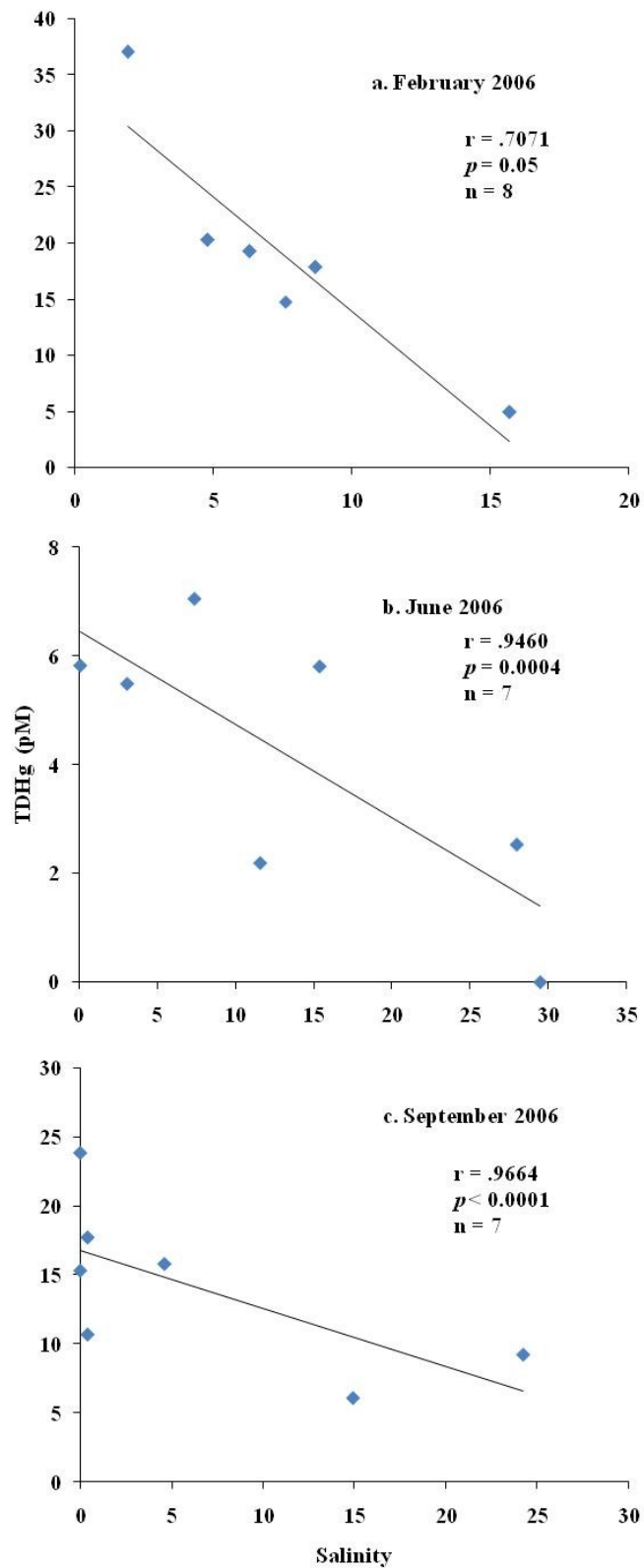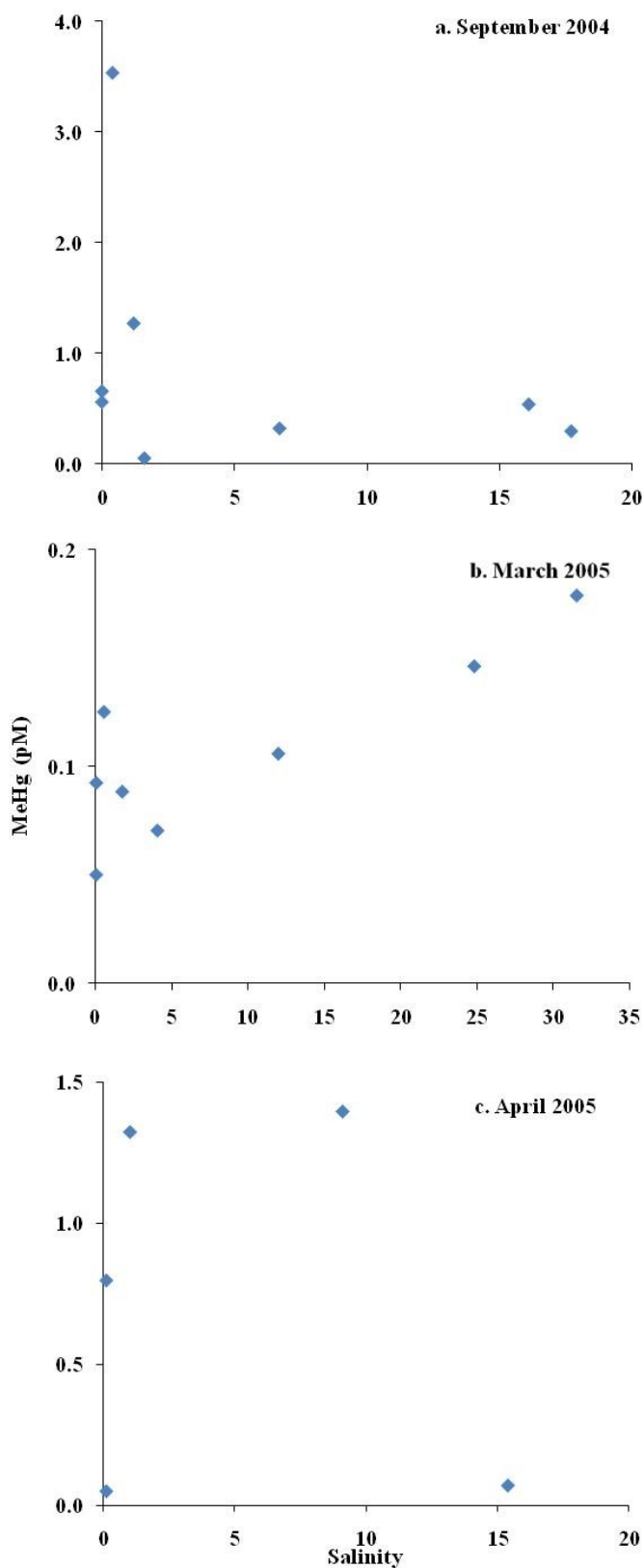
Figure 3.18. Surface water MeHg concentrations (pM) versus salinity for individual cruises during high river flow (> 300 m s^{-1}) regime.
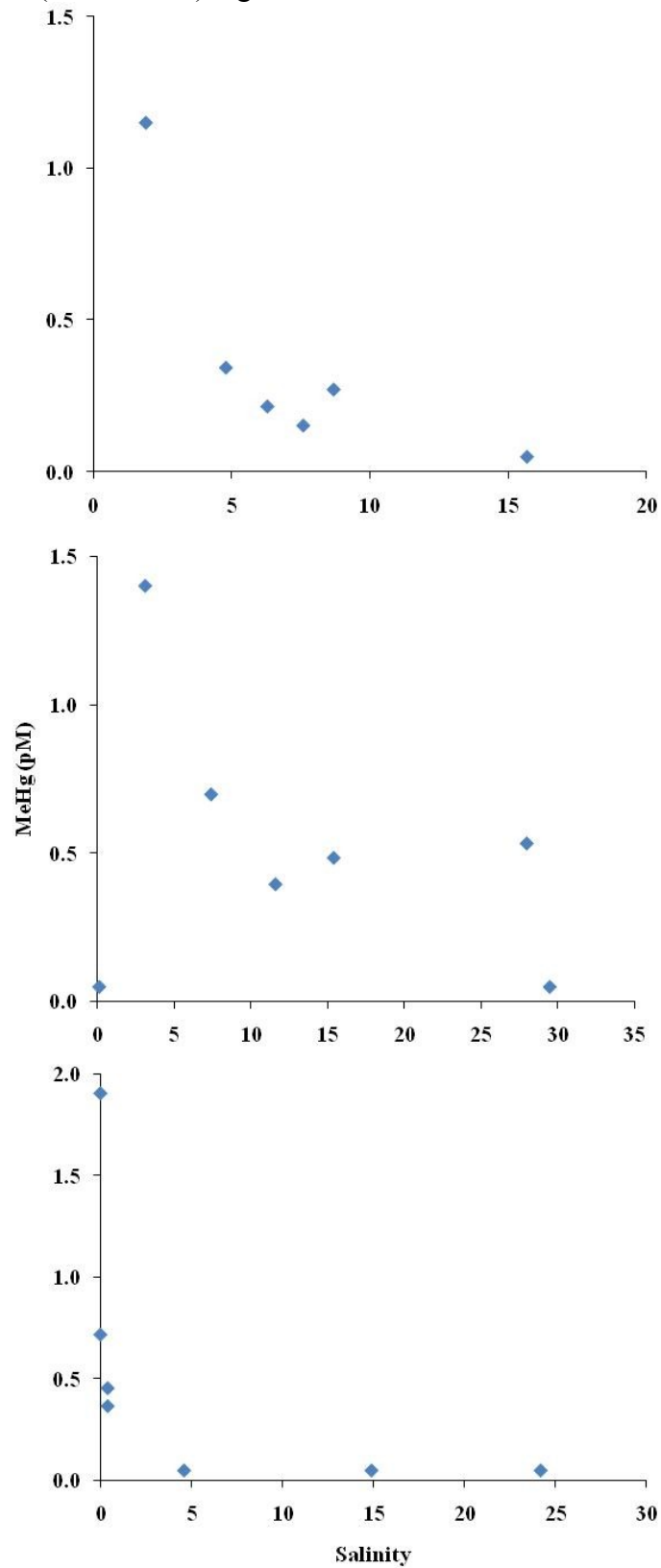
Figure 3.19. DOC concentrations (μM) versus salinity in surface waters of the Cape Fear River estuary from NAV to M18 from July 2004 to September 2006.
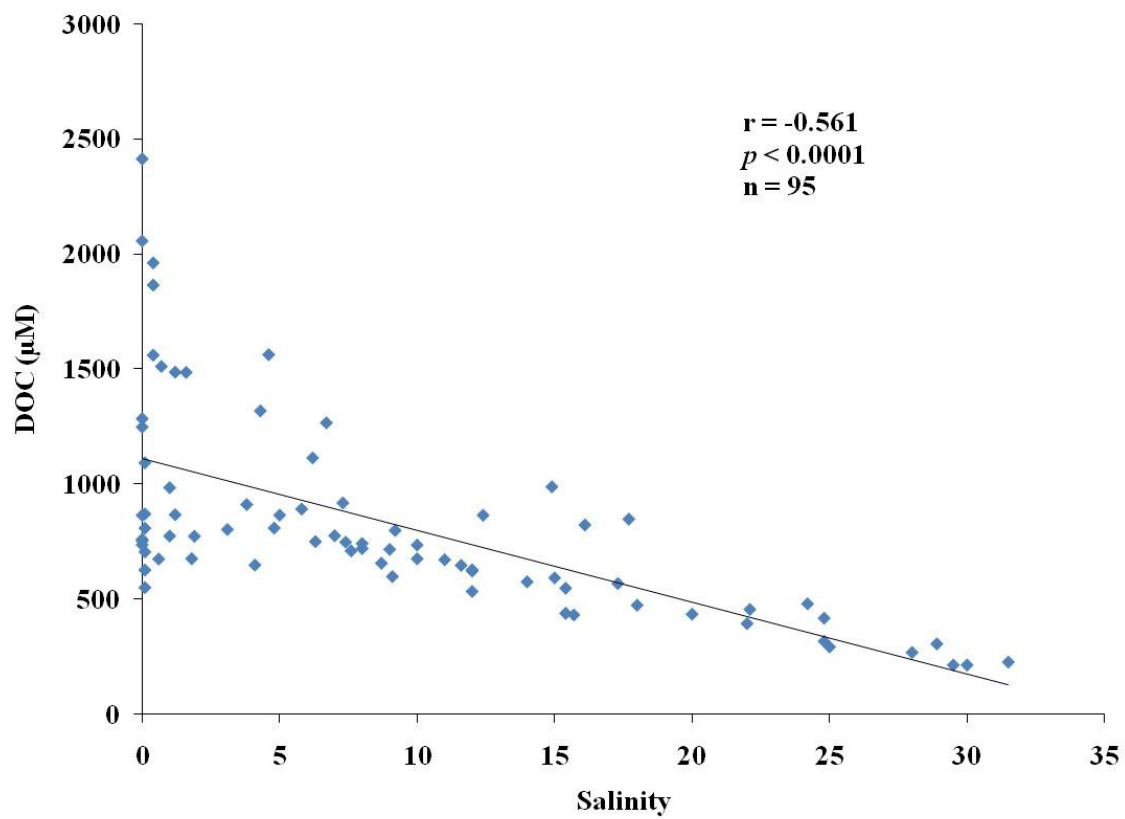
Riverine DOC is mixed conservatively with seawater and that any sources or sinks of DOC are small relative to the large inputs at the freshwater end of the estuary. Hg_{part} and MeHg were also positively correlated with DOC (Table 3.4). This correlation indicates that scavenging by organic material may control removal of TDHg and MeHg in the water column (Benoit et al., 1998; Conaway et al., 2003). It has been suggested by others (Stordal et al., 1996; Benoit et al., 1998; Conaway et al., 2003; Han et al., 2006) that the processes that control DOC cycling in estuaries may also influence Hg cycling.

Hg_{part} was highly correlated with TSS in the estuary unlike TDHg and MeHg (Table 3.4). The distribution of Hg_{part} has been explained as a function of suspended particulate matter in the San Francisco Bay estuary (Choe et al. 2003; Conaway et al. 2003), the Seine (Coquery et al. 1997), and the Scheldt estuary (Leermakers et al. 1995). Concentrations of TSS were not correlated with salinity (Figure 3.20) suggesting TSS is not simply diluted but rather there are additional sources and/or sinks throughout the estuary. Removal of Hg_{part} can occur at the turbidity maximum. The lack of correlation between TSS and MeHg has also been seen in the New York/New Jersey Harbor Estuary (Balcolm et al. 2007) where no consistent pattern between total MeHg and TSS was found, suggesting that particle scavenging or release is not a primary factor driving their concentrations in the estuary.

Concentrations of the various Hg species did not correlate with temperature at the time of sampling indicating no seasonal variation in Hg concentrations (Table 3.4). Studies in the San Francisco Bay (Conaway et al., 2003) report higher concentrations of total and dissolved Hg in the winter and spring, but attribute these increases to increased riverine discharge that occurs during these time periods. In the Patuxent River (Benoit et al., 1998), San Francisco Bay (Conaway et al., 2003), Mugu Lagoon (Rothenberg et al., 2008) and

Figure 3.20. TSS concentrations (mg/L) versus salinity in the surface waters of the Cape Fear River from NAV to M18 from July 2004 to September 2008.
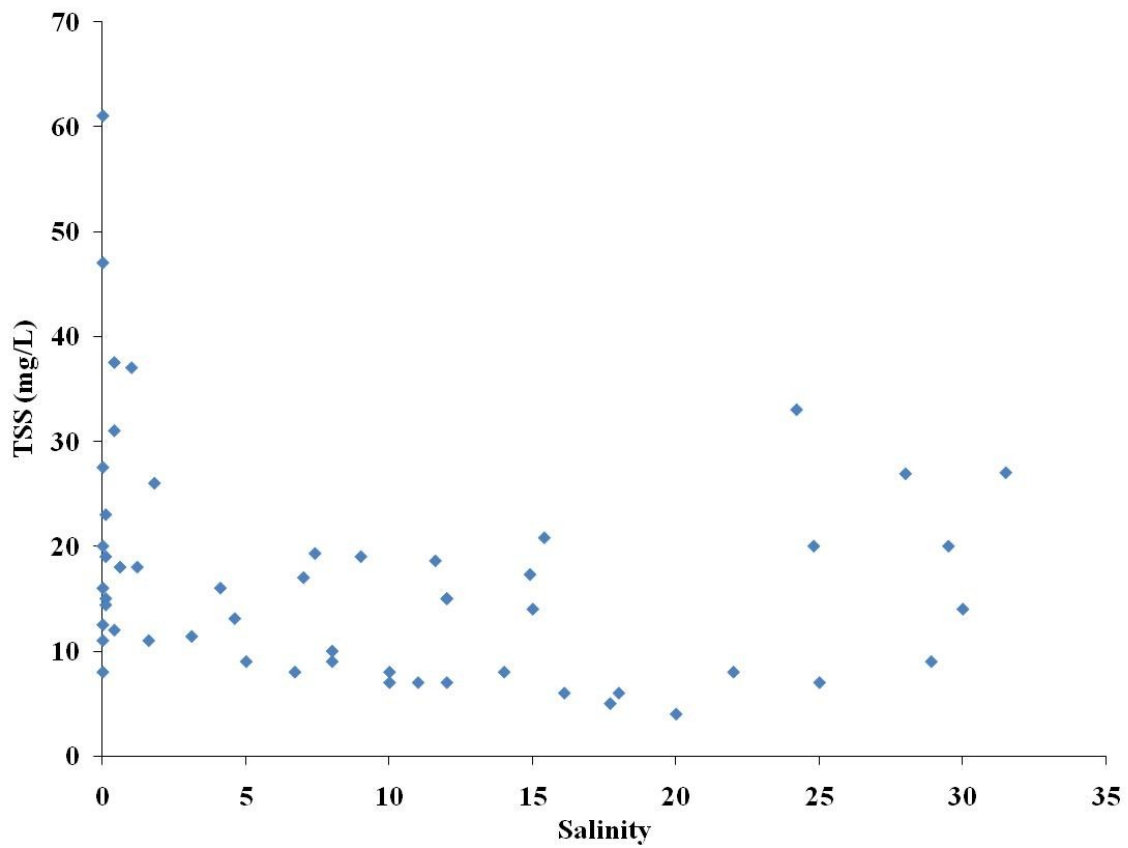
Scheldt estuary (Leermakers et al., 1995), MeHg concentrations were higher in the warmer temperatures and lower salinity waters. The lack of a temperature effect on MeHg in the Cape Fear River estuary suggests minimal input of biogenerated MeHg, since this process would be temperature dependent. Moderate to warm temperatures throughout the year in southeastern NC may also eliminate seasonal influences.

Dissolved-particle interactions

The partition or geochemical distribution coefficient (K_d) is defined as the ratio of constituent concentration in the particulate phase to that in the dissolved phase (Stordal et al., 1996). Partition coefficients were calculated for Hg via the following equation:

$$K_d = \frac{S}{D}$$

where S = concentration of Hg sorbed to particles (pmoles mg^{-1}) calculated as particulate Hg (pmoles L^{-1}) / TSS (mg L^{-1}) and D = dissolved Hg concentration (pM) (Kim et al., 2004). Log K_d values in the Cape Fear River Estuary ranged from 3.4 to 6.2 for TDHg with an average of 5.5 ± 0.5 (Table 3.7). The partition coefficients for MeHg ranged from 3.8 to 5.8 with an average of 4.8 ± 0.6 during 2 cruises in the estuary (Table 3.7). These partition coefficients for TDHg and MeHg fall within the range found in other estuaries in the US and were relatively constant throughout the estuary (Table 3.8) (Leermakers et al., 1995; Coquery et al., 1997; Benoit et al., 1998; Mason and Sullivan, 1998; Quemerais et al., 1998; Mason et al., 1999; Conaway et al., 2003). The log K_d values for TDHg are negatively correlated with TSS concentrations ($p < 0.001$, r = -0.4254, n = 95) (Figure 3.21), whereas log K_d values for MeHg were not correlated with TSS (Figure 3.22). The negative slope of the TDHg vs. TSS correlation reflects Hg_{part} normalized to TSS.   The inverse correlation between the K_d of Hg and TSS has also been seen in other estuaries and has been attributed to the "particle

Table 3.7. Average log K_d values and standard deviations in the Cape Fear River Estuary for TDHg (June 2004 to September 2006, n = 3 to 7) and MeHg (June and September 2006, n=2). NA = not analyzed.

Station	log Kd TDHg	Log Kd MeHg
NC11	5.1 ± 0.3	NA
LVC	4.8 ± 1.0	NA
AC	5.3 ± 0.3	NA
DP	5.3 ± 0.3	NA
IC	5.3 ± 0.3	NA
NAV	5.1 ± 0.5	NA
HB	4.8 ± 0.3	5.8 ± 0.6
M61	5.0 ± 1.4	4.8 ± 0.3
M54	4.9 ± 0.2	4.3 ± 0.7
M42	4.8 ± 0.5	4.8 ± 0.6
M35	4.7 ± 0.7	4.5 ± 0.6
M23	5.1 ± 0.5	5.1 ± 0.9
M18	4.7 ± 0.5	4.6 ± 0.7
SPD	5.1 ± 0.6	NA

Table 3.8.   log K_d values for Hg and MeHg for Cape Fear River estuary and various estuaries. NA = not analyzed.

Location	log Kd Hg	log Kd MeHg	Reference
NYNJ Harbor	5.3 – 6.5	4.5 – 5.6	Balcolm et al. (2008)
Chesapeake Bay	5.3 – 4.9	NA	Mason et al. (1999)
San Francisco Bay	4 – 7	NA	Conaway et al.(2003)
Patuxent River	4.8 – 5.7	3.8 – 4.0	Benoit et al. (1998)
St Lawrence River	5.5 ± 0.5	NA	Quermerais et al. (1998)
Loire River	5.5 ± 0.3	NA	Coquery et al. (1997)
Seine River	5.9 ± 0.3	NA	Coquery et al. (1997)
Texas Estuaries	4.6 – 5.2	NA	Stordal et al. (1996)
Chesapeake Bay	5.1 – 5.5	4.1 – 5.4	Lawson et al. (2001b)
Scheldt Estuary	5.3 – 6.0	NA	Leermakers et al. (1995)
Cape Fear River Estuary	3.4 – 6.2	3.8 – 5.8	Present Study

Figure 3.21. log K_d Hg versus TSS(mg/L) in surface waters for TDHg of the Cape Fear River estuary from NAV to M18 from July 2004 to September 2006.
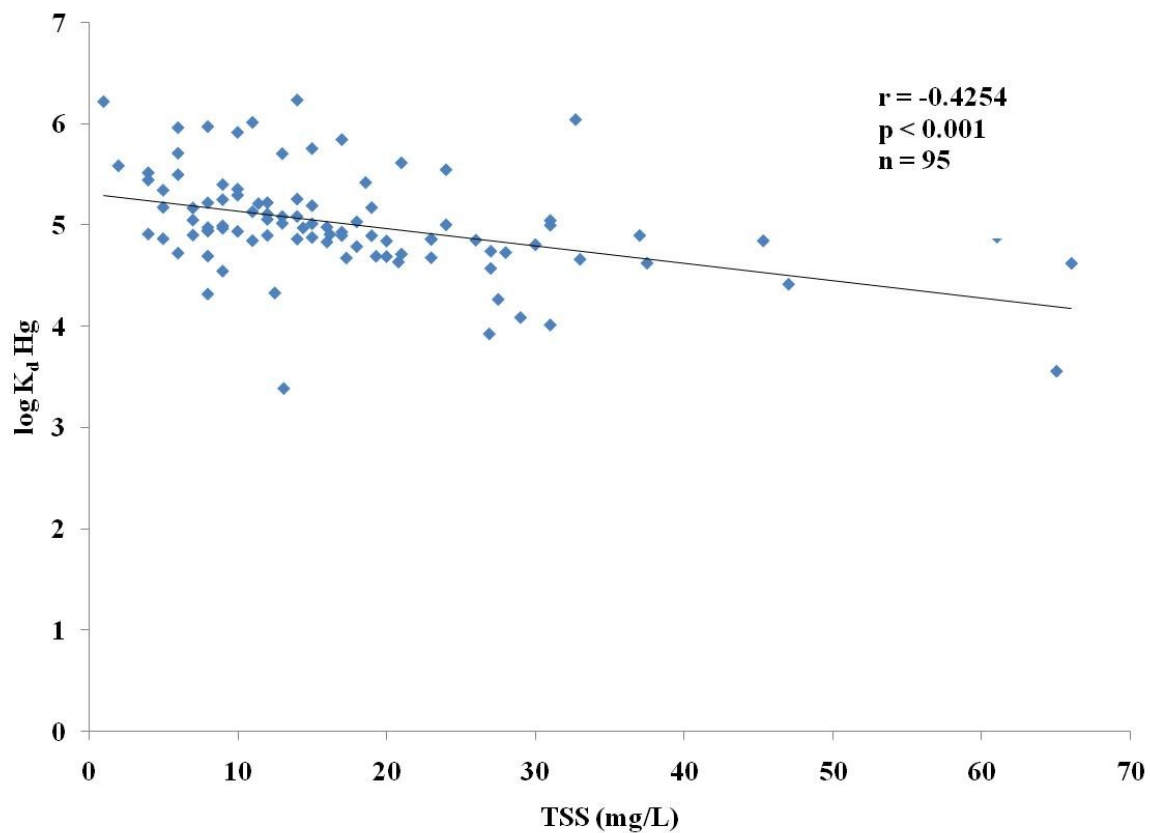
Figure 3.22. log K$_d$ MeHg versus TSS(mg/L) in surface waters of the Cape Fear River estuary from NAV to M18 from July 2004 to September 2006.
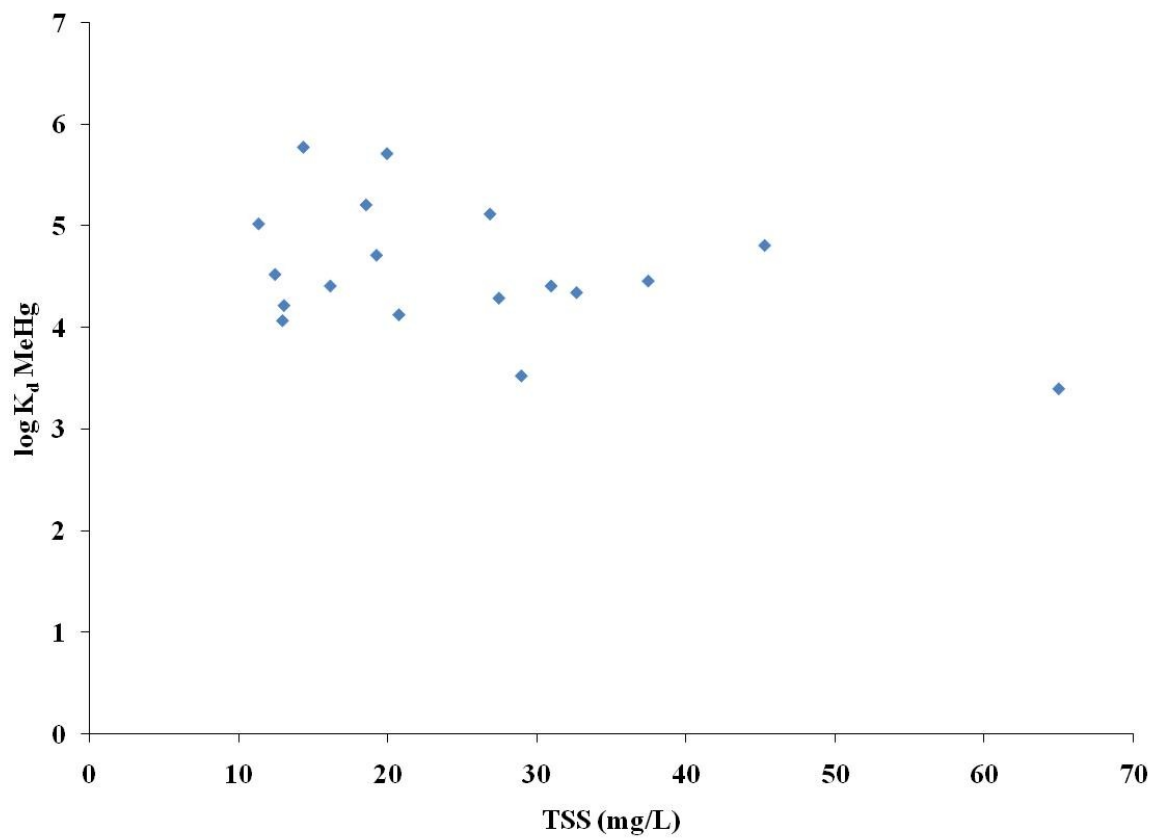
concentration effect". This occurs when the concentration of colloids in the filtrate increases as the concentration of particulate matter increases (Honeyman and Santschi, 1988; Benoit et al., 1994). Thus, K_d calculations can be affected by the presence of colloids that are included in the nominally defined "dissolved" fraction (typically $0.2 – 0.45$ μm). Stordal et al. (1996) calculated K_d values on dissolved (< 1 kDa) samples in three Texas estuaries without colloids and found that partition coefficients did not vary with the concentration of suspended particulate material. In this study, samples were filtered through 0.2 μm filters and may have contained some colloidal material. Therefore a significant fraction of TDHg may occur in colloids whereas MeHg is mainly dissolved.

Similar log K_d values between the Cape Fear River and other estuaries (Table 3.8) suggests that a southeaster blackwater estuary is not very different in terms of the partitioning of dissolve and particulate Hg. This implies that geographic location is not important in the distribution between dissolved and particulate phases.

Distribution of Hg Species – Bottom Waters

Distributions of TDHg and Hg_{part} in bottom waters of the Cape Fear River Estuary are illustrated in Figures 3.23 and 3.24. Concentrations in bottom and surface waters for TDHg were similar throughout the estuary, with the exception of M35 where bottom water concentrations were approximately 50% higher than those at the surface. Hg_{part} concentrations in the bottom and surface waters were also similar for stations from M61 to M42. At stations M35 to M18, Hg_{part} elevated concentrations were found with increasing salinities. Elevated concentrations of particulate Hg may be due to resuspension of sediment rather than the release of dissolved constituents (Mason et al. 1999). Similar surface and bottom water concentrations for total Hg with occasional elevated bottom water

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Figure 3.23. Distribution of total dissolved Hg in the bottom mainstem Cape Fear River Estuary. Each station represents the average concentration (pM) for 5 sampling cruises. Error bars represent the standard error.
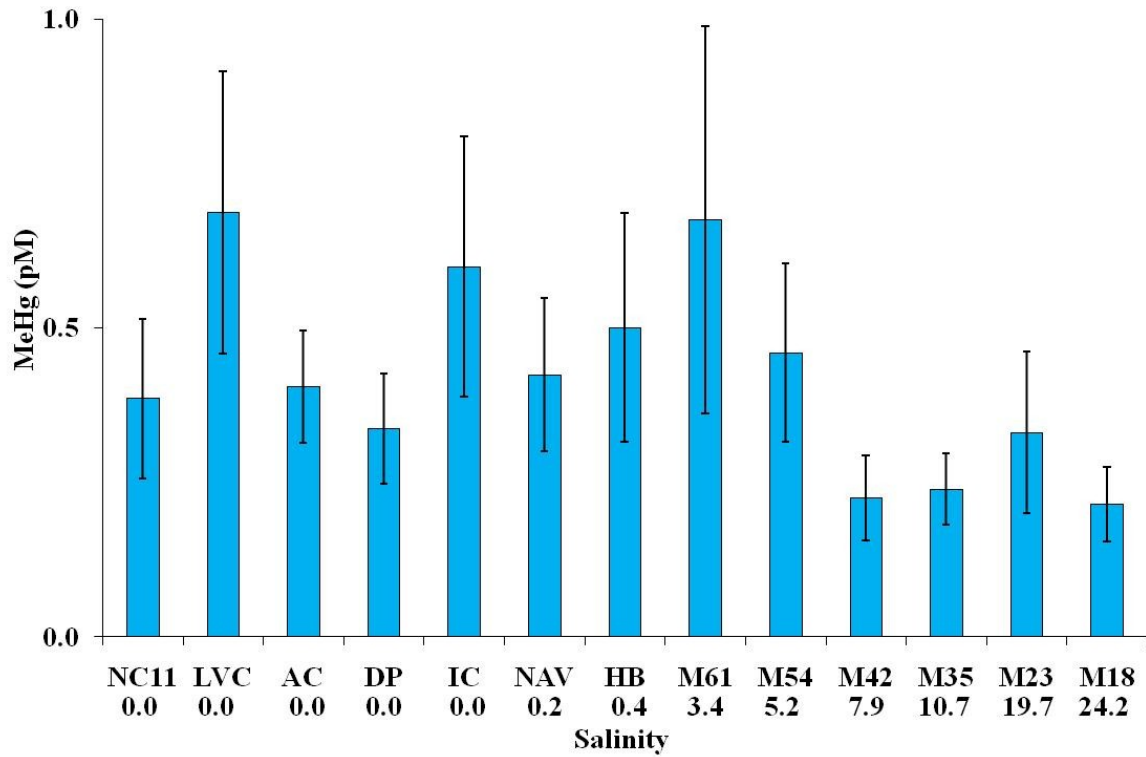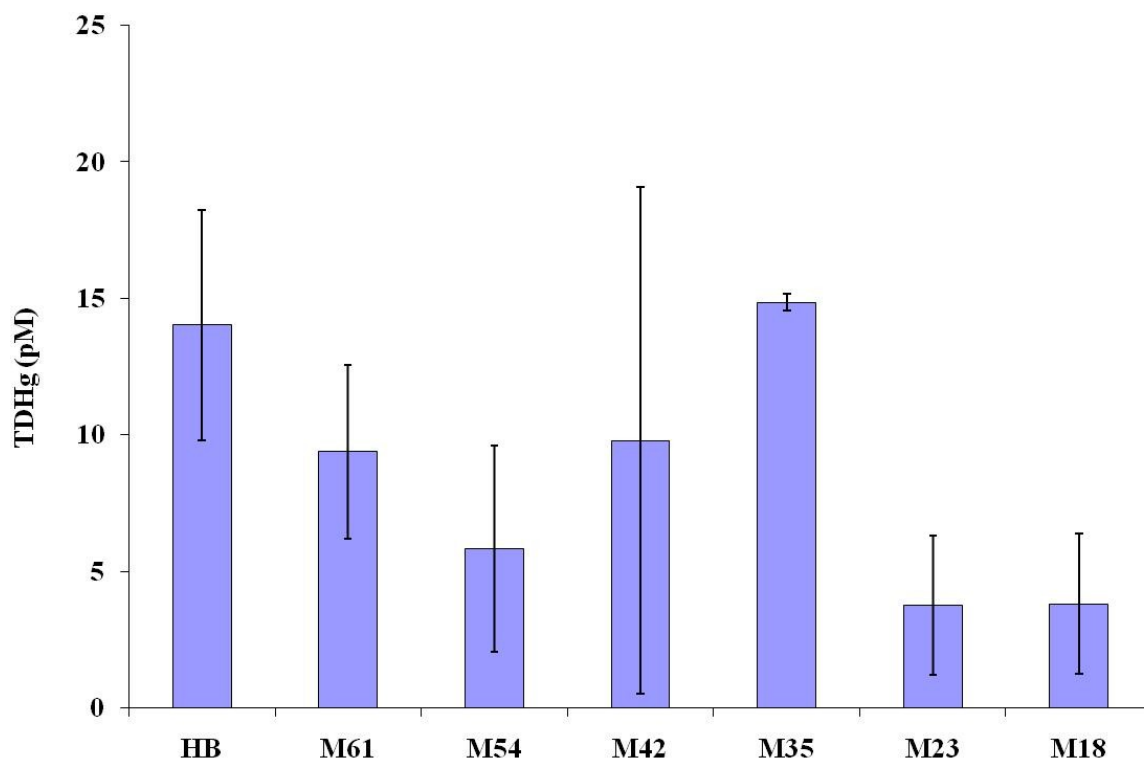
Figure 3.24. Distribution of particulate Hg in the bottom mainstem Cape Fear River Estuary. Each station represents the average concentration (pM) for 5 sampling cruises. Error bars represent the standard error.
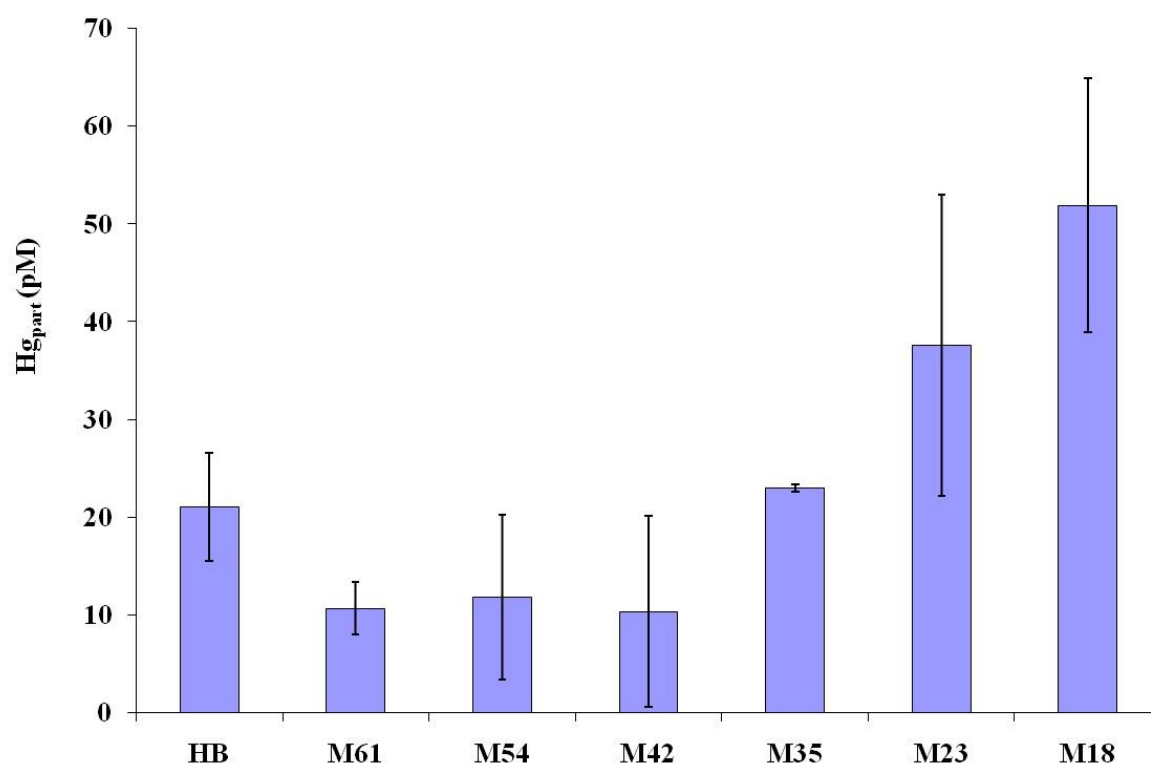
concentration was observed in the NY/NJ Harbor (Balcolm et al. 2007). Sedimentation is an important removal process of Hg_{part} from the estuary, while resuspension and mixing of bottom waters may be a potential source of Hg to surface waters (Mason et al., 1999).

Distributions of MeHg and $MeHg_{part}$ in the bottom waters of the Cape Fear River are illustrated in Figures 3.25 and 3.26. Concentrations of MeHg in bottom waters were similar to those at the surface throughout the estuary. Concentrations of $MeHg_{part}$ in bottom waters were lower than surface water concentrations at the three stations sampled. Due to the paucity of particulate Hg data in the bottom waters of the Cape Fear River, it is difficult to assess any trends that may exist. The only correlations in bottom water samples were inverse relationships between TDHg and temperature and between salinity and DOC (Table 3.9). Elevated concentrations of Hg and MeHg have been reported in regions of anoxia in lakes (Bloom et al. 1991; Hurley et al. 1991) and in the Chesapeake Bay (Mason et al. 1999). This does not appear to be the case in the Cape Fear River, where bottom waters are oxic and elevated concentrations of TDHg and MeHg are not evident.

SUMMARY

Hg concentration and speciation in the Cape Fear River estuary are similar to other estuaries that are moderately impacted. In the freshwater portion of the Cape Fear River, a defunct chlor-alkali plant is a local source of TDHg in the water column downstream from the plant. Distribution of TDHg and MeHg in the estuary and their correlation with DOC suggest that scavenging with organic material may control the removal of these two species in the estuary. Unlike TDHg and MeHg, Hg_{part} correlated with the amount of suspended material in the estuary. This correlation indicates that estuarine processes that affect the removal of suspended material in the estuary will also control the distribution of particulate

Figure 3.25. Distribution of dissolved MeHg in the bottom mainstem Cape Fear River Estuary. Each station represents the average concentration (pM) of 2 sampling cruises. Error bars represent the standard error.
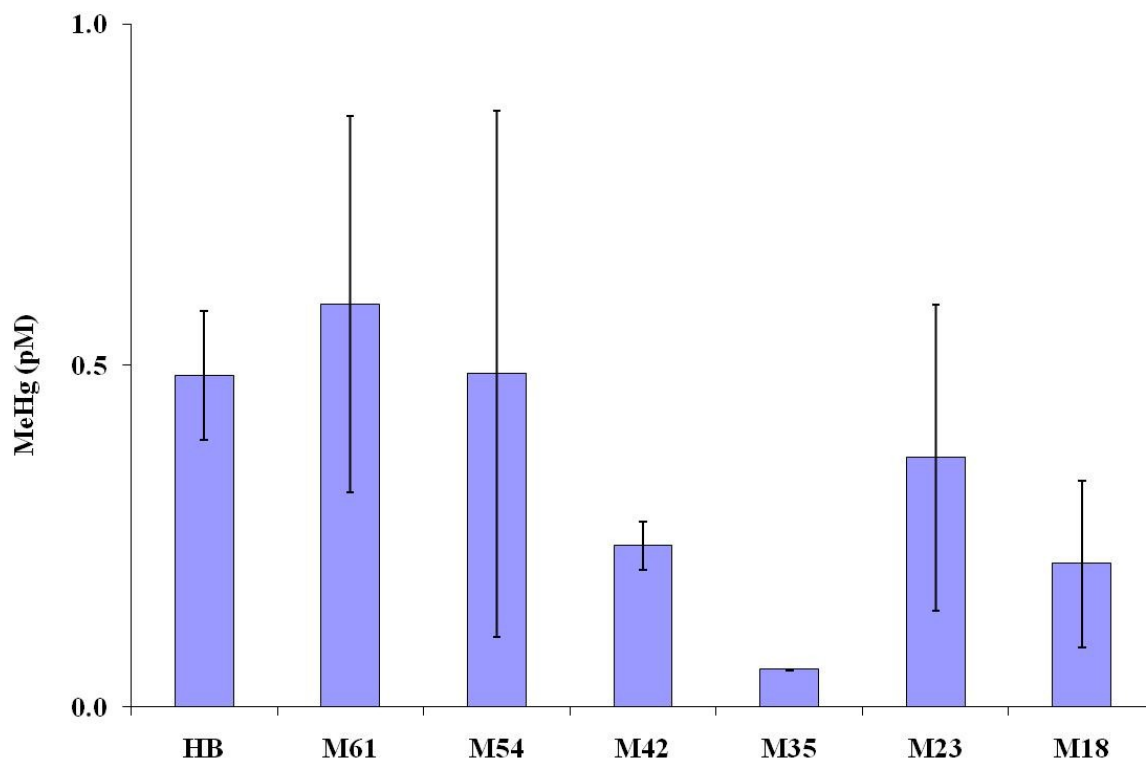
Figure 3.26. Distribution of particulate MeHg in the bottom mainstem Cape Fear River Estuary. Each station represents the average concentration (pM) of 2 sampling cruises. Error bars represent the standard error.
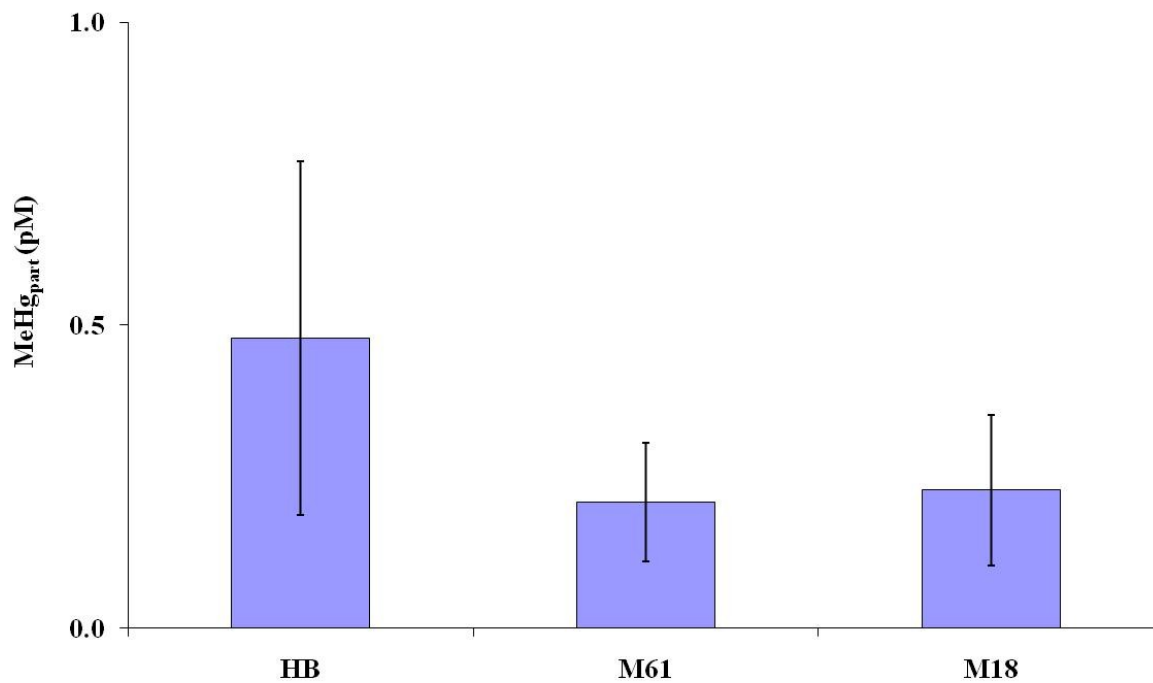
Table 3.9. Pearson Correlation results for the various Hg species and ancillary parameters in Cape Fear River Bottom waters. Sequence of numbers in each box represents *p* value, r value and n.

	Hg part	MeHg	MeHg part	Temp	S	DOC	TSS	chla
TDHg	0.521 -0.132 26	0.269 0.221 27	0.003 0.953 6	<0.0001 -0.669 27	0.236 -0.236 27	0.081 0.348 26	0.268 0.541 6	0.324 -0.873 6
Hg part		0.678 -0.086 26	0.362 -0.457 6	0.856 0.037 26	0.015 0.474 26	0.077 -0.361 25	0.978 0.015 6	0.339 0.861 3
MeHg			0.052 0.807 6	0.581 -0.109 28	0.013 -0.465 28	0.013 0.470 27	0.216 0.592 6	0.681 -0.480 3
MeHg part				0.043 -0.825 6	0.256 -0.552 6	0.040 0.833 6	0.090 0.744 6	0.551 -0.649 3
Temp					0.990 -0.003 28	0.505 0.134 27	0.591 -0.280 6	0.214 0.944 3
S						<0.0001 -0.714 27	0.922 0.052 6	0.284 0.902 3
DOC							0.529 0.326 6	0.191 -0.955 3
TSS								0.751 0.382 3
chla								

Hg. Bottom water concentrations of the various Hg species were similar to those found in surface waters of the estuary with occasional elevated bottom water concentrations. Elevated concentrations are most likely due to sediment resuspension. River flow plays an important role in the distribution of the various Hg species in the Cape Fear River Estuary. During periods of high flow, concentrations of particulate and MeHg are elevated throughout the estuary while TDHg concentrations are low. Under mid flow conditions, TDHg concentrations are the greatest.

Chapter 4 – Benthic Flux of Hg and MeHg

INTRODUCTION

Sediments play a critical role in the biogeochemical cycling of Hg. Most Hg that

enters estuarine systems that is not reduced to elemental Hg is scavenged and ultimately

buried within the sediments (Gagnon et al., 1996; Baeyens et al., 1998; Mason et al., 1999;

Choe et al., 2003; Conaway et al., 2003; Hammerschmidt and Fitzgerald, 2004; Sunderland

et al., 2004; Sunderland et al., 2006; Rothenberg et al., 2008). The sequestration of Hg in

coastal sediments may remove Hg from the water column, but it also can create a pool of Hg

that is available for methylation. Sulfate reducing bacteria are principally responsible for

MeHg production in coastal sediments (Compeau and Bartha, 1985; Gilmour et al., 1992;

King et al., 1999), and accounts for the majority of Hg that is bioaccumulated (Sager, 2002;

Hammerschmidt and Fitzgerald, 2004; Sunderland et al., 2006). MeHg production is optimal

near oxic - anoxic transitions zones that are commonly found close to the sediment-water

interface. MeHg is produced and accumulates within the sediments in active areas of sulfate

reduction. MeHg concentrations are highest below the sediment-water interface and decrease

with depth (Benoit et al., 1999; Choe et al., 2004; Hammerschmidt and Fitzgerald, 2004;

Fitzgerald et al., 2007)

Since sediments are a sink for inorganic Hg and an environment conducive to the

production of MeHg, it is important to assess if the Hg sequestered in these sediments can be

released back in to the water column. Contaminants, such as Hg species, in sediments can be

transferred to and from the water column by diffusion and advection, adsorption and desorption following sediment resuspension, and bioturbation (Mason et al., 1999).

There are three approaches used to examine sediment-water exchange of Hg species, including estimation of diffusive fluxes using porewater measurements (Choe et al., 2004; Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2008), benthic fluxes based on sediment incubation experiments (Benoit et al., 1998) and *in situ* measurements using benthic chambers (Gill et al., 1999; Covelli et al., 2008). There have been relatively few studies on the benthic flux of Hg from coastal sediments. A number of these benthic flux studies suggest that the flux of Hg is controlled by processes occurring at the sediment-water interface (Covelli et al., 1999; Gill et al., 1999; Heyes et al., 2006). MeHg fluxes are affected by the oxygen content of overlying waters where under conditions of anoxia fluxes of MeHg increases relative to oxic conditions (Baeyens et al., 1998; Covelli et al., 1999; Gill et al., 1999; Mason et al., 1999). The flux of inorganic Hg appeared to be unaffected by oxygen content of overlying waters (Baeyens et al., 1998; Covelli et al., 1999; Gill et al., 1999; Mason et al., 1999).

Chapter Objectives

1. Determine sediment concentrations of Hg at various sites throughout the Cape Fear River Estuary.

2. Determine the benthic flux of Hg and MeHg from sediments at two stations in the Cape Fear River Estuary.

METHODS

Sediment Collection and Analysis

Sediment was collected from various stations in the Cape Fear River estuary using a box corer on the research vessel R/V *Cape Fear* and using a PONAR grab sampler on small boats operated by the Lower Cape Fear River Program. Once collected, the sediment was sub-sampled using trace metal clean polypropylene cups. Three polypropylene cups were filled with the top 2-3 cm of bottom sediment at each site. Sediment samples were double bagged and kept on ice until transported back to the laboratory.

Hg Analysis

Total Hg content in sediments of the Cape Fear River estuary was determined using EPA method 1631 acid digestion and BrCl oxidation (EPA, 2001a). Approximately 0.5 to 1.5 grams of wet sediment was weighed out into 30 mL Teflon® vials. Concentrated trace metal grade HCl (8.0 mL) and concentrated trace metal grade HNO_3 (2.0 mL) was added to each vial. Samples were capped and allowed to digest at room temperature for at least 4 hours. After digestion, samples were diluted to 25.0 mL with Milli-Q water. Samples were shaken vigorously and allowed to settle until the supernatant was clear. Once settled, 500 μL of diluted digestate was pipetted into 100 g Milli-Q water. One mL of BrCl reagent was added to each sample and the sample was allowed to oxidize for 30 minutes. Samples were then immediately analyzed by CVAFS as described in Chapter 2.

% Organic Carbon

Sediments used for Hg analysis were also analyzed for loss on ignition and water loss. Triplicate samples were prepared with approximately 3 g of wet sediment per dish. Sediment was weighed out into aluminum drying dishes and put into an oven at 60°C

overnight for water loss measurement. The samples were then muffled at 550°C to determine percentage mass loss, which is taken to represent the organic content of the sediment. These values were divided by the conversion factor of 1.7 to give %OC (BS7755, 1995).

Benthic Flux Experiments

Benthic fluxes of TDHg and MeHg were measured using a core incubation technique described by Burdige and Homstead (1994), modified for trace metals as described in (Skrabal et al., 1997). In this approach, a 1m^2 box corer deployed off UNCW's 19 m research vessel, the R/V *Cape Fear*, was used to collect undisturbed bottom sediments in the estuary. The box cores were carefully subcored using trace metal clean acrylic core tubes (~26 cm long, ~14 cm diameter). Four cores were taken at each site with approximately 15 cm of sediment collected in each core. The tops and bottoms of the cores were internally sealed with polyethylene caps and the bottom of each core was externally sealed with a manually tightened rubber gasket to prevent water leakage.

Sealed cores were transported back to the laboratory where they were placed in an environmental chamber in the dark to replicate ambient light at *in situ* temperature. Unfiltered bottom water was collected at each station in polyethylene carboys and covered in black plastic bags to minimize exposure to light during transport. Bottom water was collected using a clean pumping system consisting of a Kynar® sampling tube connected to an all-plastic air-operated sampling pump. The inlet end of the sampling tubing was attached to a PVC-encased weight, which was lowered to the desired sampling depth using a nylon rope attached to the tubing.

Within 24 hours of return to the laboratory, the overlying water of each core was flushed three times with unfiltered bottom water using a peristaltic pump. The water level in

the cores was adjusted to 7 to 10 cm above the sediment surface, with a slight space left between the overlying water level and the core top. The volume of water overlying the core was approximately 1.2 to 1.9 L. A trace metal clean acrylic core (14 cm diameter, 50-60 cm in length) without sediment was filled with unfiltered bottom water and used for the recharge water during the experiments. Recharge water is defined as water used to replace water removed from the core containing sediment at each sampling time point. Filtered air, passing through gold prefilters to remove Hg found in the air, was gently bubbled into the water overlying the core using small diameter Teflon tubing inserted through the cover plate. The air gently mixed the water and maintained its O_2 concentration at near-ambient levels, with negligible loss of CO_2 (Burdige, 1993).

Samples of water overlying the core were removed as a function of time over 5 days using a peristaltic pump fitted with trace-metal clean C-flex tubing and plastic connectors. Samples were filtered during collection through 0.2 μm Meissner Stylux polyethersulfone membrane capsule filters. Withdrawn volumes from the cores were replaced with equal volumes of bottom water from the recharge core. Analyte concentrations in the bottom estuary water used to recharge the cores were also monitored during the course of the experiment. Samples were taken for TDHg, MeHg and DOC at each sampling time point, and analyzed by methods described in Chapter 2.

RESULTS

Total Hg in Sediments of the Cape Fear River

Concentrations of total Hg in the surface sediments of the Cape Fear River estuary are summarized in Table 4.1. These concentrations are similar to those found in other moderately impacted estuaries (Table 4.2). Total Hg concentrations in the sediments were

Table 4.1. Total Hg (ng Hg / g dry sediment) concentrations in the sediments of the Cape Fear River Estuary and Hg concentrations (μg / g C) normalized to carbon content of sediments. Standard deviations based on n =3. NA = not analyzed.

Date	Station	Salinity	Temp	ng Hg / g sediment	%OC	μg Hg / g C
July 2004	NC11	0	30.3	35 ± 2	2 ± 0	3 ± 0.5
	LVC	0	29.9	89 ± 3	6 ± 0	15 ± 0.4
August 2004	NC11	0	27.4	61 ± 22	2 ± 0.5	18 ± 5
	LVC	0	27.3	152 ± 40	8 ± 0.2	58 ± 31
April 2005	HB	0.1	16.8	499 ± 105	4 ± 0.2	131 ± 19
	M61	2.9	17.4	248 ± 12	2 ± 0.9	114 ± 32
	M42	2.0	17.4	38 ± 7	0.5 ± 0.4	164 ± 198
	M23	19.4	17.2	11 ± 5	0.1 ± 0.07	218 ± 142
	M18	16.1	NA	16 ± 3	0.1 ± 0.06	182 ± 69
June 2005	HB	4.4	24.6	160 ± 93	2 ± 0.4	141 ± 127
	M61	9.6	25.0	208 ± 83	2 ± 0.1	137 ± 107
	M42	8.7	25.4	22 ± 7	0.3 ± 0.2	88 ± 65
	M23	22.2	25.5	16 ± 13	0.4 ± 0.1	38 ± 22
	M18	22.1	26.4	29 ± 11	0.1 ± 0.5	39 ± 30
September 2005	HB	0.8	27.0	230 ± 81	10 ± 0.4	30 ± 24
	M61	6.3	27.3	72 ± 64	3 ± 0.6	24 ± 12
July 2007	HB	5.9	26.1	52 ± 2	4 ± 0.05	12 ± 2
	M61	14.5	26.2	42 ± 4	4 ± 0.9	14 ± 0.3
May 2008	M61	3.5	22.9	23 ± 7	2 ± 1.2	15 ± 7

Table 4.2. Comparison of surface sediment Hg concentrations (ng Hg/ g sediment) in the Cape Fear River Estuary with other estuarine systems.

Location	THg (ng Hg/g sediment)	Reference
Bay of Fundy, Canada	10 - 140	Sunderland et al. (2006)
Long Island Sound, NY	43 – 345	Hammerschmidt and Fitzgerald (2004)
San Francisco Estuary, CA	100 - 350	Conaway et al. (2003)
Baltimore Harbor, MD	341	Mason and Lawson. (1998)
Patuxent River, MD	100 - 140	Benoit et al. (1998)
Lavaca Bay, TX	5 – 783	Bloom et al. (1999)
Hudson River, NY	699	Heyes et al. (2004)
St. Lawrence River	66 – 320	Holmes and Lean (2006)
Chesapeake Bay, MD	80 - 180	Mason et al. (1999)
Cape Fear River, NC, USA	11 - 499	Present Study

variable, but were consistently higher in the more organic-rich sediments on the Cape Fear River. Inorganic Hg concentrations in the mainstem estuary are significantly correlated with % organic carbon (%OC) (Figure 4.1, r = 0.9644, $p < 0.001$). At the freshwater stations, LVC sediment concentrations (89 and 152 ng Hg/g sediment) were double than those found 9 km upstream at NC11 (35 and 61 ng Hg/g sediment) during both samplings. Sediment concentrations in the mainstem Cape Fear River were greatest at stations HB and M61 (23 – 499 ng Hg/g sediment) and decreased (11 – 38 ng Hg/g sediment) downstream as the composition of sediments became less organic-rich.   Lowest sediment Hg concentrations occurred at M23 even though M18 is more seaward and has higher salinity and lower organic carbon content.

Inorganic Hg concentrations were also normalized to organic carbon content of the sediments to take into account grain size differences (Table 4.1). When normalized to organic carbon content of the sediments, Hg concentrations were less variable between stations. At LVC, normalized concentrations were still elevated compared to concentrations at NC11.

Benthic Flux of TDHg and MeHg

Benthic flux experiments for TDHg and MeHg were conducted at M61 and HB to examine the effects of increased Hg concentrations found in the sediments at these stations on overlying water column concentrations. Fluxes were measured using a core incubation technique that captures exchange resulting from diffusion and bioirrigation.   Processes such as advection and tidal pumping are not taken into account by this method. The core incubation technique has the advantage of directly measuring net fluxes including processes occurring at the sediment-water interface.

Figure 4.1. Relationship between Hg concentrations and %OC in sediments of the mainstem Cape Fear River Estuary in April and June 2005.

r = 0.9644
p < 0.0001
n = 10

% Organic Carbon

Hg (ng Hg/g sediment)
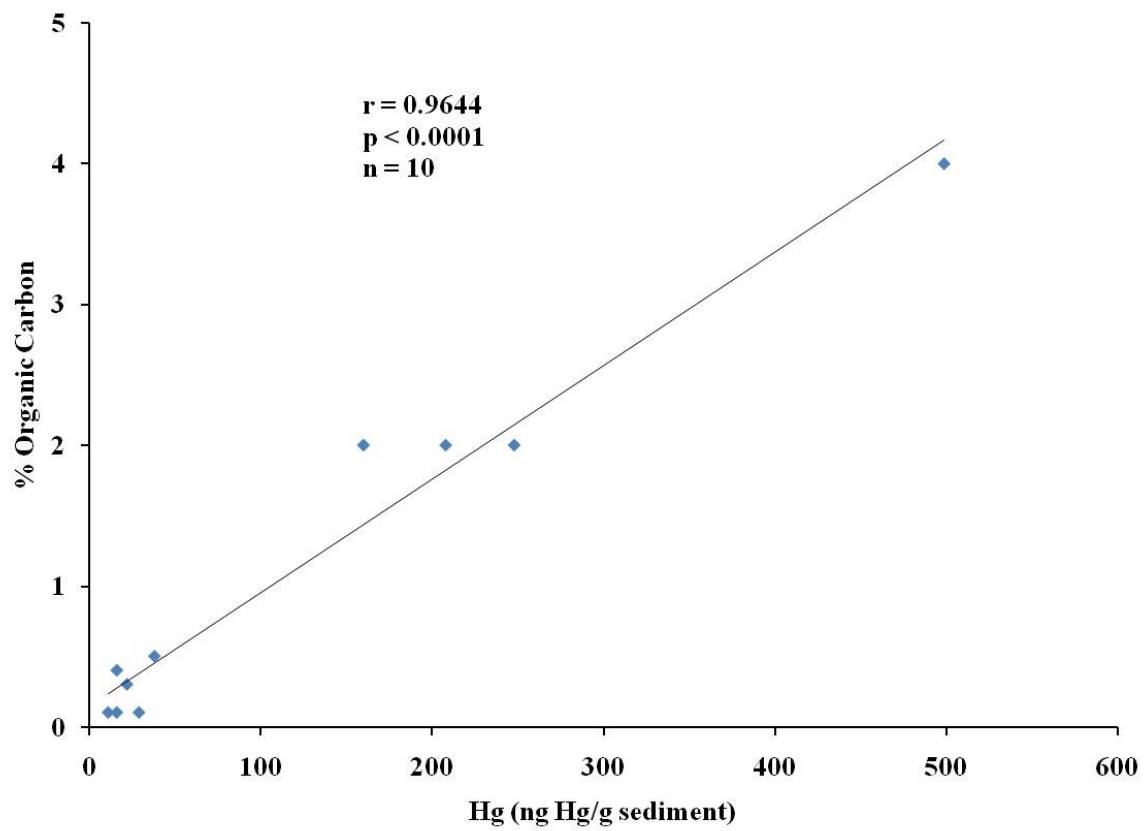
Fluxes measured using this technique were considered different from zero if the linear regression of corrected concentrations vs. time produced a statistically significant fit ($p \leq$ 0.05). When flux calculations yielded $p > 0.05$, they were reported as a zero net flux. Experimental results from each experiment used in the statistical analysis of fluxes are found in Figures 4.2 to 4.7. Results from core incubation experiments for TDHg and MeHg conducted at M61 and HB are presented in Tables 4.3 and 4.4. Negative values indicate a flux into sediments from overlying water and positive values indicate a flux out of sediments into the water column. Total dissolved Hg fluxes at stations M61 and HB ranged from -4800 to 760 and -1200 to 2500 pmol m^{-2} d^{-1}, respectively. Fluxes of MeHg ranged from -22 to 0 and from -32 to 0 pmol m^{-2} d^{-1}, respectively at M61 and HB. There was spatial and temporal variability of benthic fluxes for both Hg species at both stations. This variability of flux measurements in the Cape Fear River estuary is not uncommon, as it has been observed in other estuaries (Table 4.5). At station M61, the benthic fluxes of TDHg, MeHg and DOC were measured during 4 experiments (Table 4.3). At M61, three fluxes out, five fluxes in and four non measurable fluxes or TDHg. For MeHg, only 2 out of 12 fluxes showed significant flux in. DOC fluxes were also highly variable. Of 9 cores, outward fluxes were measured for three cores, one flux in and five net zero fluxes.

At station HB, benthic fluxes of TDHg were measured during 5 experiments while, MeHg and DOC were measured during 4 experiments (Table 4.4). TDHg fluxes out of the sediment were measured in 3 cores, fluxes in were measured in 4 cores and 8 cores showed no net flux. Of 12 cores, there was only 1 significant flux into the sediments for MeHg.

Figure 4.2. Corrected TDHg concentrations (pM) for flux experiments conducted at M61. Each figure shows TDHg (pM) in water for three cores with sediment (M61A, M61B and M61C) and one core containing unfiltered water (Recharge) against time (hours).
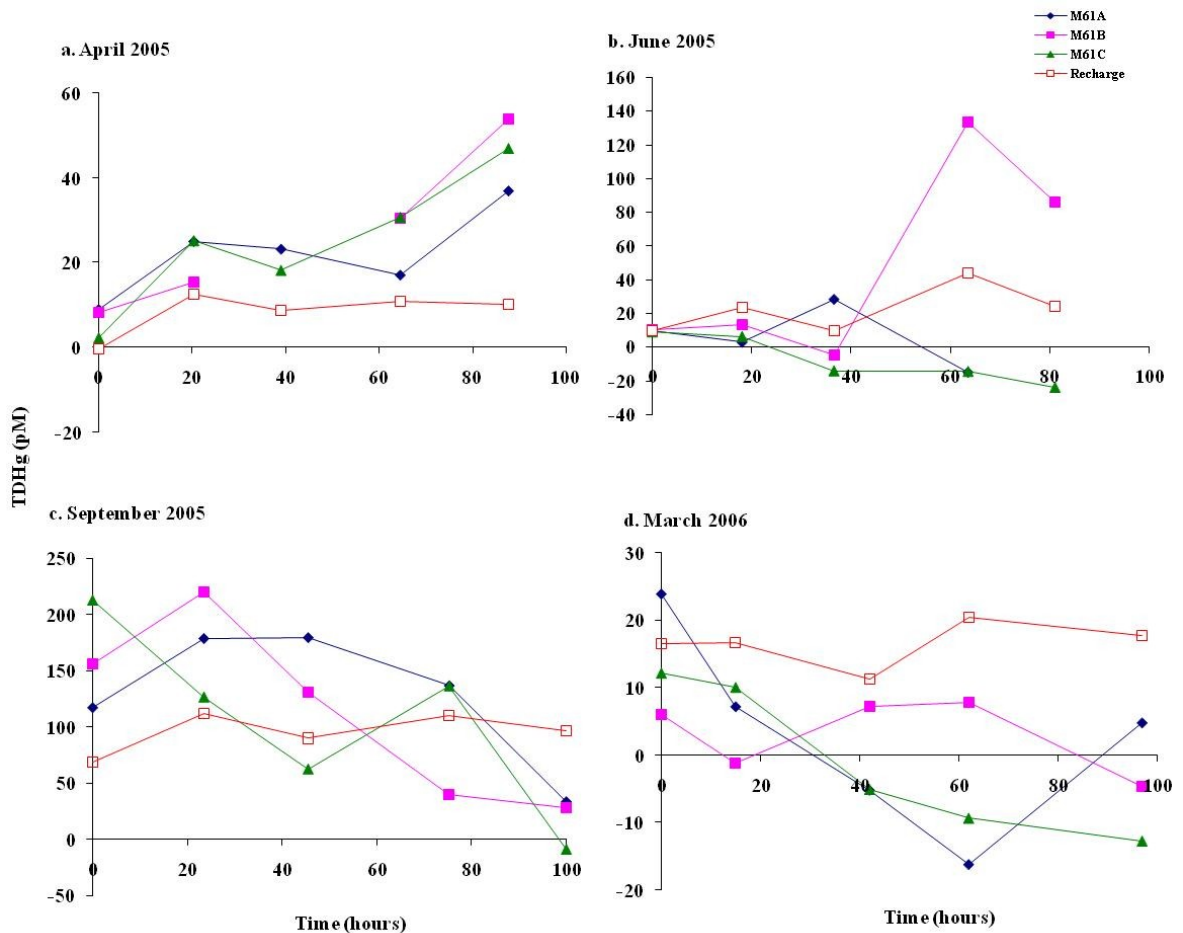
Figure 4.3. Corrected MeHg concentrations (pM) for flux experiments conducted at M61. Each figure shows MeHg (pM) in water for three cores with sediment (M61A, M61B and M61C) and one core containing unfiltered water (Recharge) against time (hours).
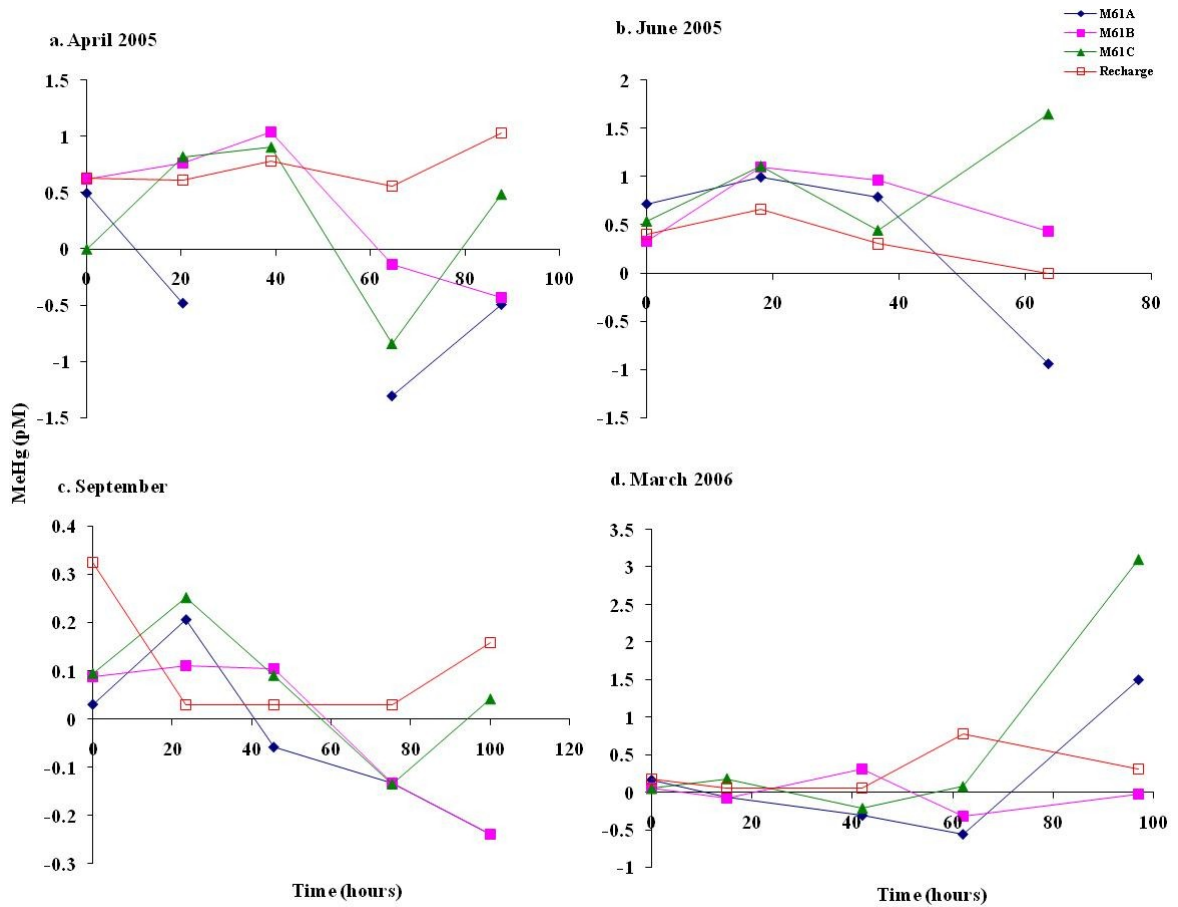
Figure 4.4. Corrected DOC concentrations (μM) for flux experiments conducted at M61. Each figure shows DOC (μM) in water for three cores with sediment (M61A, M61B and M61C) and one core containing unfiltered water (Recharge) against time (hours).
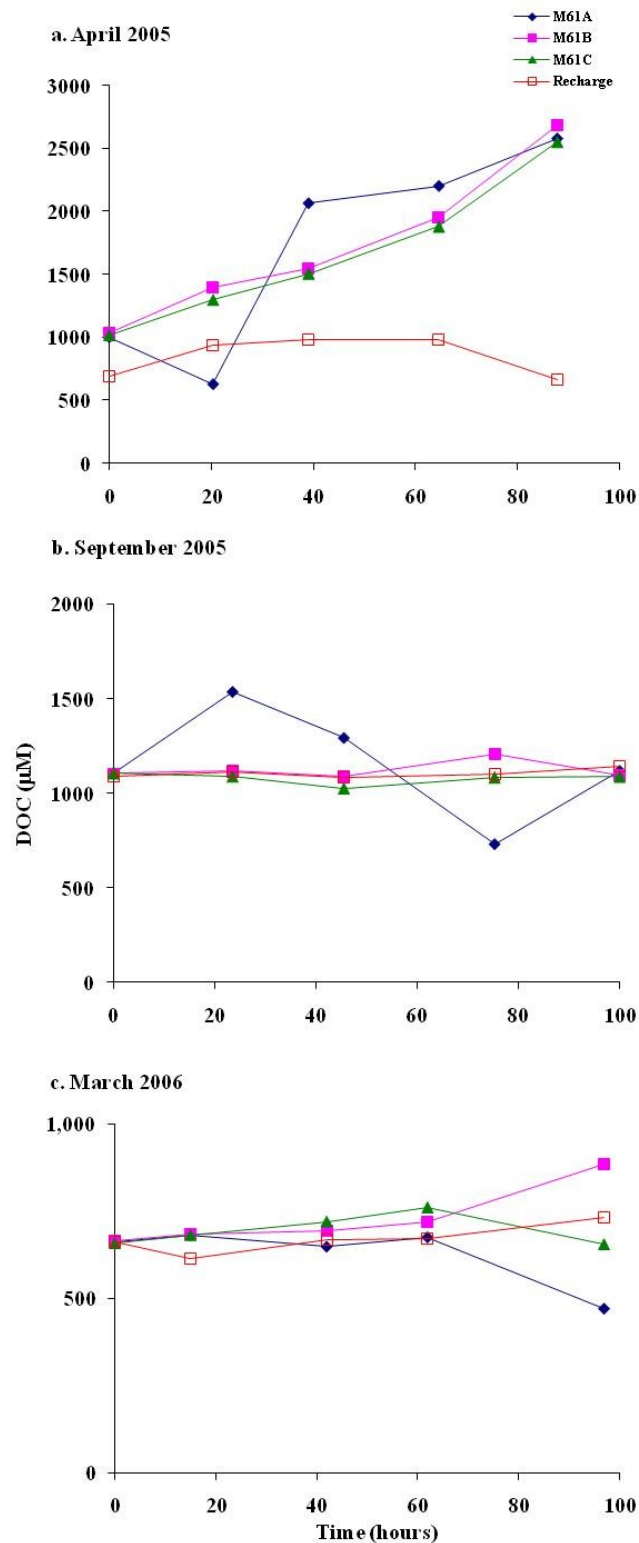
Figure 4.5. Corrected TDHg concentrations (pM) for flux experiments conducted at HB. Each figure shows TDHg (pM) in water for three cores with sediment (HBA, HBB and HBC) and one core containing unfiltered water (Recharge) against time (hours).
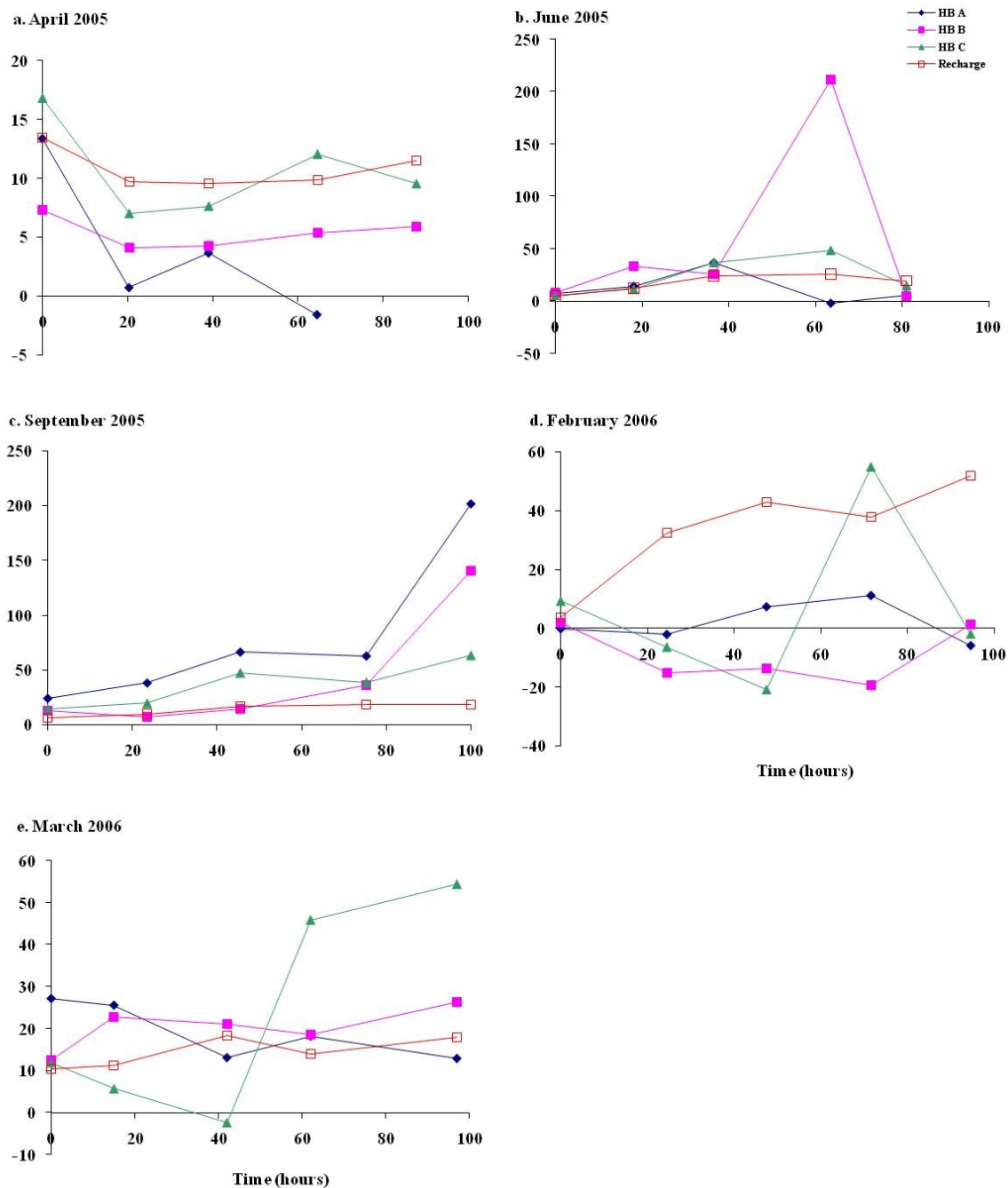
Figure 4.6. Corrected MeHg concentrations (pM) for flux experiments conducted at HB. Each figure shows MeHg (pM) in water for three cores with sediment (HBA, HBB and HBC) and one core containing unfiltered water (Recharge) against time (hours).
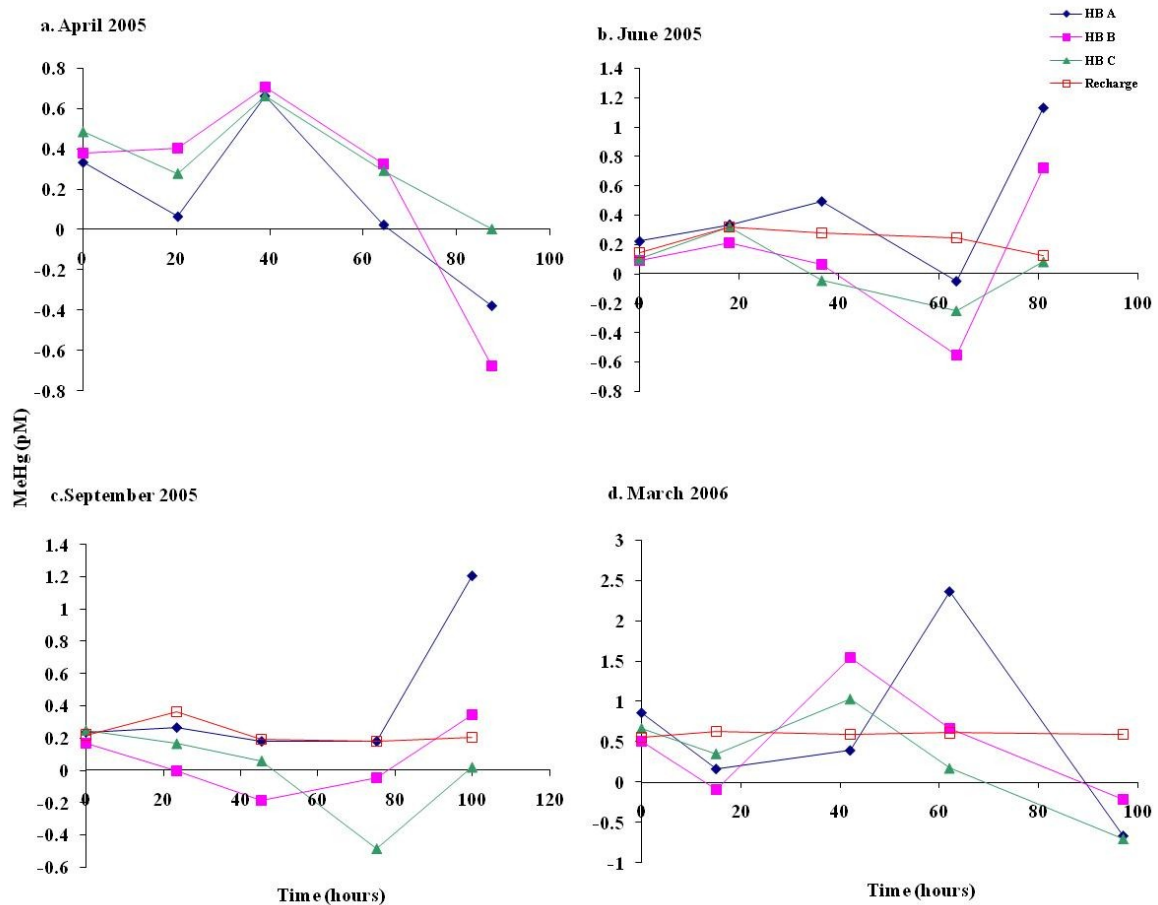
Figure 4.7. Corrected DOC concentrations (µM) for flux experiments conducted at HB.
Each figure shows DOC (µM) in water for three cores with sediment (HBA, HBB and HBC)
and one core containing unfiltered water (Recharge) against time (hours).
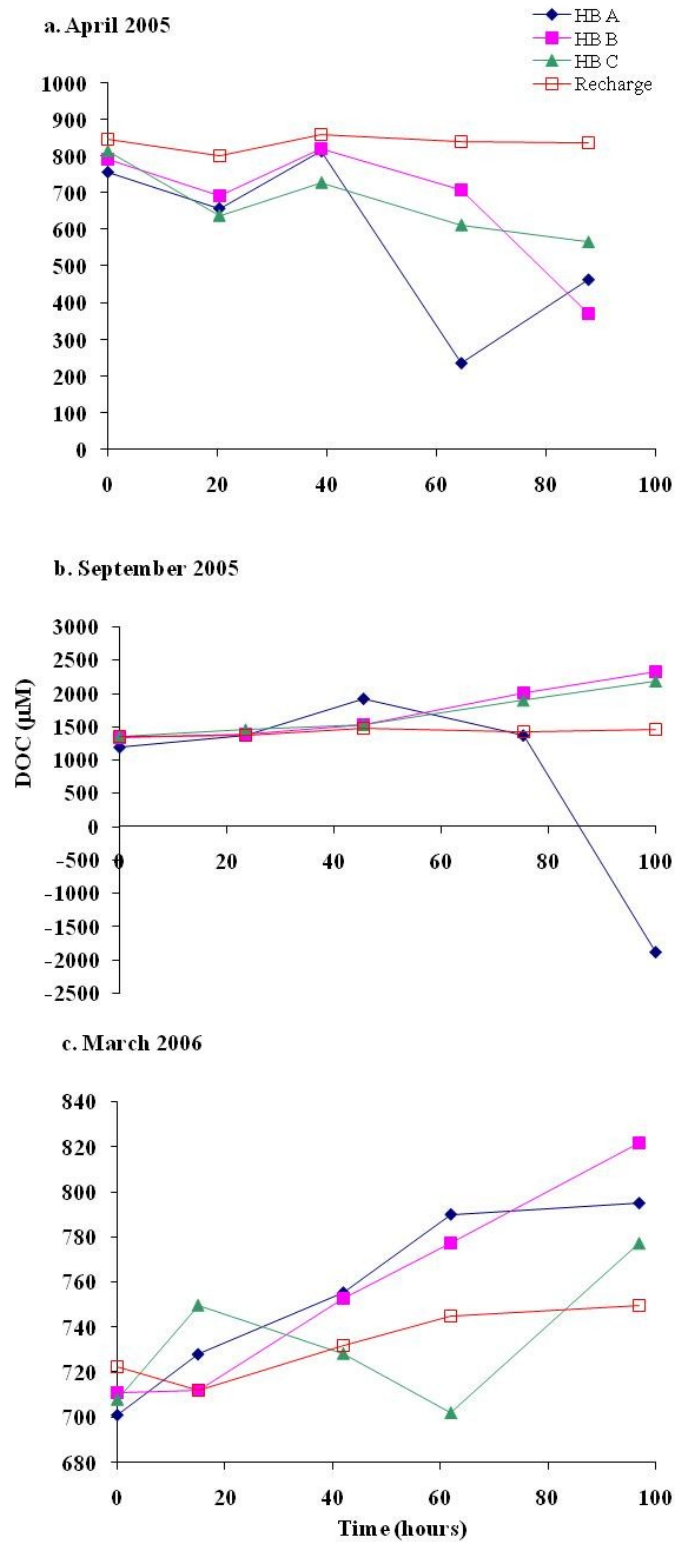
Table 4.3. Benthic Flux measurements for TDHg, MeHg and DOC for individual core measurements at station M61 in the Cape Fear River Estuary at each sampling date. Negative numbers indicate a flux into the sediment. Positive values indicate a flux out of the sediment. Non-statistically significant fluxes are represented as "0" net flux. n = number of cores per sampling site.
p = level of significance. NA = not analyzed. Sediment concentration of total Hg in ng Hg / g sediment and %OC for each sampling.

Sampling Date	TDHg Fluxes (pmol m^{-2} d^{-1})	MeHg Fluxes (pmol m^{-2} d^{-1})	DOC Fluxes (mmol m^{-2} d^{-1})	ng Hg / g sediment	%OC
6 April 2005 n = 3	230 ($p < 0.05$) 720 ($p <0.05$) 760 ($p < 0.02$)	0 -22 ($p < 0.01$) 0	40 ($p < 0.02$) 30 ($p < 0.005$) 40 ($p < 0.001$)	248 ± 12	2 ± 1
7 June 2005 n = 3	0 0 -960 ($p < 0.01$)	0 0 0	NA	208 ± 83	2 ± 0.1
21 September 2005 n = 3	0 -4200 ($p < 0.02$) -4800 ($p < 0.05$)	0 -6 ($p < 0.01$) 0	0 0 0	72 ± 64	3 ± 0.6
24 March 2006 n = 3	-1100 ($p < 0.01$) 0 -520 ($p < 0.02$)	0 0 0	0 0 -1.2 ($p < 0.02$)	NA	NA

Table 4.4. Benthic Flux measurements for TDHg, MeHg and DOC for individual core measurements at station HB in the Cape Fear River Estuary at each sampling date. Negative numbers indicate a flux into the sediment. Positive values indicate a flux out of the sediment. Non-statistically significant fluxes are represented as "0" net flux. n = number of cores per sampling site. p = level of significance. NA = not analyzed. Sediment concentration of total Hg in ng Hg / g sediment and %OC for each sampling.

Sampling Date	TDHg Fluxes (pmol m^{-2} d^{-1})	MeHg Fluxes (pmol m^{-2} d^{-1})	DOC Fluxes (mmol m^{-2} d^{-1})	ng Hg / g sediment	%OC
6 April 2005 n = 3	0 0 0	-32 ($p < 0.05$) 0 0	0 0 0	499 ± 105	4 ± 0.2
7 June 2005 n = 3	0 0 0	0 0 0	NA	160 ± 93	2 ± 0.4
21 September 2005 n = 3	2500 ($p < 0.05$) 2100 ($p < 0.05$) 710 ($p < 0.05$)	0 0 0	0 19 ($p < 0.005$) 16 ($p < 0.005$)	230 ± 81	10 ± 0.4
10 February 2006 n = 3	-1000 ($p < 0.01$) -1100 ($p < 0.02$) 0	NA	NA	NA	NA
24 March 2006 n = 3	-640 ($p < 0.02$) 0 -1200 ($p < 0.001$)	0 0 0	2 ($p < 0.02$) 2 ($p < 0.001$) 0	NA	NA

Table 4.5. Comparison of benthic flux of TDHg and MeHg in the Cape Fear River Estuary with other estuarine systems. Fluxes are reported in pmol m^{-2} d^{-1}. . Negative numbers indicate a flux into the sediment. Positive values indicate a flux out of the sediment. NA = not analyzed. ND = not detectable.

Location	TDHg	MeHg	Method	Reference
NY/NJ Harbor	NA	8 to 126	Porewater Profiles	Hammerschmidt et al (2008)
Baltimore Harbor	-67 to 240	0 to 50	Benthic Chambers	Mason et al (2008)
Saguenay Fjord, Canada	518 to 4909	NA	Porewater Profiles	Gagnon et al (1996)
St. Lawrence River	NA	-8 to 50	Porewater Profiles	Holmes and Lean (2006)
Long Island Sound, NY	NA	24 to 174	Porewater Profiles	Hammerschmidt et al (2004)
Patuxent River and Baltimore Harbor	59 to 845	ND	Mesocosms	Benoit et al (1998)
Gulf of Trieste	40 to 32280	-490 to 11000	Porewater profiles and benthic chambers	Covelli et al (1999)
Lavaca Bay, TX	ND	0.8 to 6000	Porewater profiles and benthic chambers	Gill et al (1999)
San Francisco Bay Delta	-1900 to 2600	-92 to 850	Porewater profiles and benthic chambers	Choe et al (2004)
Cape Fear River, NC	-4800 to 2500	-32 to 0	Sediment Cores	Present Study

Four outward fluxes and 5 zero net fluxes were measured for DOC at HB. No dependence of flux on temperature was found at either M61 or HB for any analyte.

DISCUSSION

Sediment Concentrations of Hg

Concentrations of total Hg in sediments of the Cape Fear River estuary are spatially and temporally variable. The heterogeneity of the sediments is a likely explanation for the variability of Hg concentrations found in the estuary. The normalization of Hg to organic carbon content (Table 4.1) removes some of the variability of Hg sediment concentrations in the lower estuary, but not in the freshwater stations. At LVC, downstream from the former HoltraChem site, sediment concentrations were twofold higher and %OC in sediments was three to fourfold higher than those found at NC11, a relatively uncontaminated control site. After normalization concentrations of Hg in the sediments of LVC are 3 to 5 times higher than that found at NC11. This suggests an impact on Hg concentrations in the sediments downstream from the chlor-alkali plant in relation to concentrations found upstream. The former chlor-alkali plant site may be a source of Hg to the sediments of LVC and the organic carbon of those sediments acts as a trap and retains Hg. Elevated inorganic Hg (100 ng Hg/g sediment) in the Bay of Fundy (Canada)are the result of Hg releases by a chlor-alkali plant that operated along the river (Sunderland et al., 2006). Methylation of Hg in sediments has been shown to be proportional to the concentration of bioavailable Hg-S species (Benoit et al., 1998). The presence of elevated inorganic Hg in the sediments and salinities that are conducive to sulfate production, indicate a pool of Hg that is possibly bioavailable to methylating bacteria.

Although concentrations at LVC were higher than those found at NC11, they were not the highest concentrations in the estuary. At stations M61 and HB, concentrations ranged from 23 to 455 ng Hg /g sediment. Concentrations at M61 were up to 3 times higher than those at LVC. The high correlation between Hg concentrations and % OC has been seen in the Long Island Sound (Hammerschmidt et al., 2004), NY/NJ Harbor (Hammerschmidt et al., 2008), Bay of Fundy (Sunderland et al., 2006) and Mugu Lagoon, CA (Rothenberg et al., 2008). This correlation suggests that organic matter is complexing and trapping Hg in sediments, due to the affinity of Hg to particles and sediments. It may also control the availability of dissolved inorganic Hg to methylating bacteria (Benoit et al., 1998; Hammerschmidt et al., 2008). Increased organic matter stimulates methylating bacteria in sediments (Benoit et al., 1998). Miller et al. (2007) showed that dissolved Hg is bound by sulfide and DOC, increasing the bioavailability of Hg to methylating bacteria. The relationship between organic matter and Hg concentrations in the Cape Fear River suggests that these areas are a source of MeHg to the water column. The concentrations of inorganic and MeHg in sediments correlates with one another in other estuaries (Baeyens et al., 1998; Mason and Lawrence, 1999; Hammerschmidt and Fitzgerald, 2004) although MeHg was not measured in these sediments.

Benthic Flux of TDHg and MeHg

Variable flux magnitudes and directions indicate sediments can be either a source or sink of TDHg to the water column. Pearson correlation was performed on the measured fluxes for each species and ancillary data collected at the time of core collection in order to better understand what is controlling the variability of the fluxes (Table 4.6). There were no significant correlations found between fluxes of TDHg and MeHg and any other parameter.

Table 4.6. Pearson Correlation for benthic flux experiments in the Cape Fear River. Sequence of numbers in each box represents *p* value, r value and n. S varied from 0.8 to 13.7psu. DO in bottom waters ranged from 3.0 to 9.4 mg/L.

	MeHg Flux	DOC Flux	Temp	S	DO
TDHg Flux	0.865 -0.0342 27	0.144 0.358 18	0.992 0.002 27	0.0684 -0.356 27	0.700 0.0777 27
MeHg Flux		0.701 -0.0973 18	0.703 0.0770 27	0.110 0.315 27	0.117 -0.309 27
DOC Flux			0.933 0.0212 18	0.119 -0.380 18	0.324 0.247 18
Temp				0.0498 -0.381 27	>0.0001 -0.808 27
S					0.756 0.0628 27
DO					

Results from benthic flux experiments for MeHg suggest that sediments of the Cape Fear River are not a significant source of MeHg to the water column. Benoit et al (1998) also suggested that sediments were not a source of MeHg in the Patuxent River where bottom waters are oxic. Earlier studies have suggested that the flux of total Hg and MeHg from sediment to the water column is driven by dissolution of Fe oxides or by co-transport of inorganic Hg and MeHg bound to DOC (Gagnon et al., 1996; Gill et al., 1999). This does not appear to be the case in the Cape Fear River as fluxes of total Hg and MeHg did not correlate to DOC fluxes. Other ancillary parameters, such as metals, were not measured so it is difficult to assess if these play a role in the flux of Hg from sediments. Studies on other metals in the Cape Fear River, such as Cu (Shank et al., 2004a) and Zn (Skrabal et al., 2006), however suggest benthic fluxes play a minor role in the CFRE. Most likely because it is a well flushed system which reduces accumulation of metals in pore waters.

A general consensus among flux experiments is that the fluxes of MeHg and inorganic Hg increase under hypoxic and anoxic conditions (Covelli et al., 1999; Gill et al., 1999; Hammerschmidt and Fitzgerald, 2004). Cores were kept oxic during this study by gently bubbling with Hg-free air to mimic the generally well-oxygenated water column of the Cape Fear system (Mallin et al., 2007). Bothner et al.(1998) suggested that maintaining oxygenated conditions reduces Hg fluxes to the water column. Most likely because the presence of an oxidized surface layer inhibits the transfer of Hg from the sediments to water column (Gagnon et al., 1996; Gill et al., 1999). Other processes that may affect Hg fluxes include bioirrigation and bioturbation. Earlier studies have suggested that in the absence of bioirrigation and/or bioturbation, there would be no enhanced exchange of Hg from the sediments to the water column (Choe et al., 2004; Hammerschmidt and Fitzgerald, 2004).

SUMMARY

Inorganic Hg concentrations are highly variable spatially and temporally in the sediments of the Cape Fear River. Sediment concentrations are elevated at stations LVC, M61 and HB where there appears to be geochemical trapping by organic carbon indicated by the high correlation with organic carbon in the sediments. Elevated concentrations found at LVC suggest that Hg from the chlor-alkali plant have impacted that station. Benthic fluxes are highly variable in both directions and magnitude for both inorganic and MeHg, suggesting sediments are an active part of the system, but not a consistent source or sink. MeHg was never seen to flux out of the sediments in the Cape Fear River, unlike other estuaries. The oxic water column may have inhibited the flux of MeHg and TDHg out of the sediments by formation of a metal-oxide rich interface between the water column and sediments.

Chapter 5 – Photochemical Transformations of Hg

INTRODUCTION

Three processes currently being investigated in the photochemical transformation of Hg in natural waters are reduction of divalent Hg (Hg^{2+}) to elemental Hg (Hg^0) or dissolved gaseous Hg (DGHg), oxidation of Hg^0 to Hg^{2+} and photodegradation of MeHg (MeHg). Of these processes, the photochemistry of Hg in natural waters has focused on reduction of Hg^{2+} to Hg^o observed in freshwater systems (Amyot et al., 1994; Amyot et al., 1997a; Amyot et al., 1997b; Amyot et al., 2001; Zhang and Lindberg, 2001) and seawater (Amyot et al., 1997a; Costa and Liss, 1999; Costa and Liss, 2000) as a source of Hg to the atmosphere.

Surface waters can become supersaturated with DGHg, when divalent Hg is reduced to elemental Hg. This supersaturation results in outgassing of elemental Hg to the atmosphere (Lanzillotta et al., 2002). This process has been documented in temperate and high arctic lakes (Amyot et al., 1994; Amyot et al., 1997b; Amyot et al., 1997c), as well as in simulated natural waters, and seawater (Costa and Liss, 1999; Costa and Liss, 2000). This pathway is considered one of most important process involved in photochemical transformations of Hg. Recent documentation of other photochemical transformations suggest however that there are other pathways involved in the photochemical cycling of Hg (Sellers et al., 1996; Amyot et al., 1997b; LaLonde et al., 2001; Lalonde et al., 2004).

Photo-oxidation of Hg^o has recently been suggested as a photochemical pathway that balances photo-reduction of Hg^{2+} (Amyot et al., 1997a; LaLonde et al., 2001; Zhang and Lindberg, 2001). This reaction was previously ignored since Hg^o was considered to be

unreactive (Nriagu, 1994). Photo-oxidation co-occurs with photo-reduction in surface waters, and is likely to dominate during the summer over the flux of Hg^o to the atmosphere (LaLonde et al., 2001).

Photodegradation of MeHg has also been overlooked as microbial demethylation was considered to be the dominant pathway for MeHg degradation (Sellers et al., 1996; Hammerschmidt and Fitzgerald, 2006). Earlier studies have however demonstrated that photochemical reactions lead to both degradation and production of MeHg in optically clear lakes. Photodemethylation of Hg is important because it reduces the availability of MeHg for bioaccumulation in aquatic species reducing exposure to humans. Photodegradation of MeHg is a first order reaction with respect to both concentration and photosynthetically active radiation (PAR) intensity (Hammerschmidt and Fitzgerald, 2006).

Photochemical transformations of Hg are important because their effects on speciation determine the ultimate environmental impact of Hg. The suggested cycling between divalent and elemental Hg by redox processes may facilitate methylation of Hg. Oxidation can make more Hg bioavailable leading to a greater potential for methylation and bioaccumulation. Photoreduction of divalent Hg may lead to evasion of elemental Hg from surface waters of coastal systems which represents a source of atmospheric Hg (Nriagu, 1994), and a loss from aquatic ecosystems. In addition, resuspension events may introduce Hg rich sediments to the photic zone. Irradiation of these resuspended sediments may provide an additional photochemical pathway for release of Hg species that may be sequestered in bottom sediments.

Chapter Objectives

1. Determine the effect of light on ambient particles and resuspended sediment on water column concentrations of TDHg and MeHg.

2. Determine the rate of photoproduction of dissolved gaseous Hg in the Cape Fear River Estuary.

3. Determine the rates of photochemically mediated demethylation in the Cape Fear River Estuary.

METHODS

Photochemical Experiments

Total and Methylmercury

Three treatments were used for the photochemical irradiation experiments: 1 L of unfiltered water without sediment, 1 L of filtered water without sediment and 1 L of filtered water with approximately 1 to 2.5 grams of wet estuarine sediment. Controlled photolysis experiments were performed using procedures modified from Kieber et al. (2006). Teflon® bottles, which are optically transparent for 280-800 nm wavelengths (Amyot et al., 1994), were used for photochemistry experiments to maximize light penetration and to reduce loss of Hg to the sides of the bottles. Six 1L Teflon bottles were filled using two for each treatment. A sample was collected for initial measurements of TDHg and MeHg. Three bottles were enclosed in black plastic bags to serve as dark controls. The three light bottles were placed in a constant temperature water bath (set at ambient estuarine temperature) and irradiated for 10 hours in simulated sunlight using a Spectral Energy^{TM} solar simulator (1 kW Xe arc light source) with AM1 filter to remove wavelengths not found in the solar spectrum. Treatments containing sediment were stirred throughout the experiment using a trace metal

clean Teflon coated stir bar. Dark and irradiated light bottles were filtered through 0.2 μm acid-washed Meissner capsule filters at the end of the experiment and analyzed for TDHg and MeHg to determine photochemically-induced changes in concentrations. Methods of analysis for TDHg and MeHg have been previously described in Chapter 2.

Dissolved Gaseous Hg

Dissolved gaseous Hg (DGHg) samples were unfiltered, unaltered and were processed immediately after sampling, as DGHg is not stable in solution (Lindberg, 2000). Dissolved gaseous Hg is the measurement of Hg^o naturally present in a sample; therefore no reducing agent was required for this analysis. In order to avoid the production of Hg^o as an artifact during analysis, it was crucial that the bubblers used during DGHg measurements never contained $SnCl_2$ (Manley, 2008). DGHg was analyzed using methods adapted from Mason (1994). Initial DGHg was measured on 250 mL of sample where the Hg^0 was purged from the sample using ultra-high pure (UHP) argon gas for 20 minutes. The purged Hg^o was passed through a soda lime trap to remove moisture and the Hg^0 was amalgamated onto a gold-coated sand column. The gold column was removed from the purging set-up and placed in the desorption manifold. The Hg was thermally desorbed from the gold-coated sand column using a nichrome coil controlled by a Brooks Rand Model 2 temperature controller. The coil was heated for 3 minutes to reach a temperature between 450-500º C. The Hg was then carried in an inert gas (UHP argon) stream into the quartz cell of the spectrometer for detection. Light from a low-pressure 4-W Hg vapor lamp was directed through the quartz cell at a wavelength of 253.7 nm and excited the Hg atoms which emit light at intensity proportional to the concentration of Hg passing through the cell. This emitted light passed

through a filter and into a photomultiplier tube, converting the light into an electrical signal, which was integrated by Logger Pro software.

The photoproduction of DGHg was measured on unaltered unfiltered samples that were irradiated using a solar simulator. One liter of unfiltered estuarine water was placed in a Teflon bottle and irradiated for 6 hours while an additional liter of unfiltered water was kept in the dark as a control for the same amount of time. DGHg was measured in duplicate from each treatment and analysis of DGHg was performed as described above.

Rates of Demethylation

Experiments to determine demethylation rates in the Cape Fear River were conducted following the procedures of Hammerschmidt and Fitzgerald (2006). Each experiment consisted of four treatments incubated using a solar simulator to mimic the radiation exposure of the Cape Fear River. These treatments included both filtered and unfiltered estuary water that was either irradiated or kept in the dark as a control. Each treatment was placed in a 1L Teflon bottle and spiked to a final concentration of 10 pM MeHg, ~10 times the ambient concentration of MeHg found in the Cape Fear River. All treatments were incubated at *in situ* temperature using a constant temperature water bath for 6 days. MeHg concentrations both on filtered and unfiltered treatments were determined on 0.2µm filtered aliquots initially and after 1, 3 and 6 days of incubation. Six days was chosen because this is the approximate residence time of water in the Cape Fear River estuary (Ensign et al., 2004).

RESULTS

Photochemical Transformations of Total and MeHg

A series of controlled photolysis experiments were performed to quantify the impact of irradiation on TDHg and MeHg concentrations in filtered estuarine water (Table 5.1 and

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Table 5.1. Concentrations of TDHg (pM) in filtered estuary water from Stations SPD to NAV initially (T=0), after 10 hours irradiation in the solar simulator and 10 hours in the dark.

Experiment	Date	Station	T=0	Light	Dark
1	Apr-05	M61	15.6	12.9	7.3
2	Aug-06	HB	6.1	5.5	5.9
3	Jun-07	M61	4.3	2.4	2.4
4	Jun-07	HB	1.9	1.5	1.7
5	Jun-07	M61	5.8	5.6	9.0
6	Jun-07	HB	4.8	5.4	5.8
7	Jun-07	M61	3.0	3.7	6.5
8	Jun-07	HB	2.4	3.5	6.1
9	Aug-07	HB	8.3	6.4	5.7
10	Aug-07	NAV	11.8	10.1	13.1
11	Aug-07	M18	2.7	2.2	3.3
12	Aug-07	M42	1.8	1.8	1.9
13	Aug-07	M35	2.1	2.6	2.6
14	Aug-07	SPD	3.0	3.5	3.5
15	Aug-07	M61	16.6	17.6	15.6
16	Aug-07	M23	4.3	5.3	5.5
17	Aug-07	M54	3.3	5.6	5.0
18	Feb-08	M61	9.9	9.1	8.7
19	May-08	M61	21.1	15.2	14.2
20	May-08	M61	18.6	16.9	17.1

5.2), unfiltered estuarine water containing ambient particles (Table 5.3 and 5.4) and on filtered estuarine water containing 1 – 2.5 g of wet sediment per liter (Table 5.5). Changes in Hg concentrations resulting from irradiation of the various treatments are found in Figures 5.1 – 5.5. No clear trends of increase or decrease in water column concentrations of TDHg or MeHg were apparent among the three treatments. Changes that did occur were small and variable.

Photolysis experiments were conducted on 0.2 µm filtered surface estuary water twenty times from TDHg and seven times for MeHg (Figures 5.1 and 5.2). For TDHg, there was an increase in mean TDHg water column concentrations for eight experiments, a decrease in concentrations in eleven experiments and one that showed no change. In MeHg photolysis experiments, two showed an increase, one showed a decrease and no change in MeHg concentration was found in four experiments.

The second treatment consisted of unfiltered surface estuary water to examine if irradiation of ambient particles would release total Hg and MeHg into the water column. These experiments were conducted twenty times for TDHg and seven times for MeHg (Figures 5.3 and 5.4). Photolysis of unfiltered estuary water demonstrated the same level of variability seen in the filtered treatment. For TDHg, seven showed a decrease in concentration, twelve showed an increase and one showed no change. In experiments conducted to determine change in MeHg concentration, three showed a slight increase, two showed a slight decrease and two showed no change in concentrations.

The final treatment consisted of 0.2 µm filtered estuary surface water and

Table 5.2. Concentrations of MeHg (pM) in filtered estuary water from Stations M61 and HB initially (T=0), after 10 hours irradiation in the solar simulator and 10 hours in the dark.

Experiment	Date	Station	T=0	Light	Dark
1	Apr-05	M61	0.01	0.04	0.14
2	Jul-05	M61	0.1	0.15	0.09
3	Aug-06	HB	0.14	0.19	0.13
4	Jun-07	HB	0.2	0.05	0.21
5	Jun-07	HB	0.31	0.16	0.06
6	May-08	M61	0.27	0.14	0.23
7	May-08	M61	0.25	0.32	0.31

Table 5.3. Concentrations of TDHg (pM) in filtered estuary water from Stations SPD to NAV initially (T=0), after unfiltered water was irradiated for 10 hours in the solar simulator and unfiltered estuary water was kept in the dark for 10 hours.

Experiment	Date	Station	T=0	Light	Dark
1	Apr-05	M61	15.6	6.5	4.7
2	Aug-06	HB	18.4	16.1	12.3
3	Jun-07	M61	4.3	3.5	2.8
4	Jun-07	HB	1.9	2.3	1.9
5	Jun-07	M61	5.8	7.0	5.6
6	Jun-07	HB	2.4	3.8	8.6
7	Jun-07	HB	4.8	6.7	7.6
8	Jun-07	M61	3.0	5.6	6.3
9	Aug-07	M61	16.6	12.5	24.9
10	Aug-07	M18	2.7	2.7	3.2
11	Aug-07	M42	1.8	3.0	3.1
12	Aug-07	SPD	3.0	4.5	4.2
13	Aug-07	NAV	11.8	13.4	13.9
14	Aug-07	M54	3.3	5.1	5.7
15	Aug-07	M35	2.1	4.8	3.3
16	Aug-07	M23	4.3	8.1	6.0
17	Aug-07	HB	8.3	13.0	169.5
18	Feb-08	M61	9.9	9.9	19.3
19	May-08	M61	21.1	16.0	15.0
20	May-08	M61	18.6	18.4	20.3

Table 5.4. Concentrations of MeHg (pM) in filtered estuary water from Stations M61 and HB initially (T=0), after unfiltered water was irradiated for 10 hours in the solar simulator and unfiltered estuary water was kept in the dark for 10 hours.

Experiment	Date	Station	T=0	Light	Dark
1	Apr-05	M61	0.01	0.1	0.13
2	Jul-05	M61	0.17	0.18	0.19
3	Aug-06	HB	0.26	0.31	0.25
4	Jun-07	HB 1	0.2	0.19	0.17
5	Jun-07	HB 2	0.31	0.22	0.27
6	May-08	M61 2	0.27	0.28	0.19
7	May-08	M61 1	0.25	0	0.22

Table 5.5. Concentrations of TDHg (pM) in filtered estuary water from Stations M61 and HB initially (T=0), after sediment was suspended in filtered water and irradiated for 10 hours in the solar simulator and sediment was suspended in filtered water and kept in the dark for 10 hours. Sediment concentration and % organic carbon for sediment collected at the same time as each water sample. NA = not analyzed.

			TDHg			MeHg			ng Hg/g dry sed	%OC
Experiment	Date	Station	T=0	Light	Dark	T=0	Light	Dark		
1	Apr-05	M61	15.6	5.61	4.34	0.01	0.13	0.19	248 ± 12	2
2	Jul-05	M61	NA	NA	NA	0.37	0.21	0.21	160 ± 93	2
3	Aug-06	HB	6.43	5.67	5.4	0.11	0.02	0.05	230 ± 81	10
4	Jun-07	HB	1.85	0.43	0	0.2	0.34	0	52 ± 2	4
5	Jun-07	HB	4.8	6.97	7.09	0.31	0.19	0.17	52 ± 2	4
6	Jun-07	HB	2.37	7.16	8.22	NA	NA	NA	52 ± 2	4
7	Jun-07	M61	4.29	2.29	2.57	NA	NA	NA	42 ± 4	4
8	Jun-07	M61	3.03	3.68	5.72	NA	NA	NA	42 ± 4	4
9	Jun-07	M61	5.75	4.91	8.63	NA	NA	NA	42 ± 4	4
10	May-08	M61	18.61	16.72	17.56	0.27	0.17	0	23 ± 7	2
11	May-08	M61	21.1	12.79	14.05	0.25	0.28	0.28	24 ± 5	2

Figure 5.1. Changes in TDHg (pM) concentration and standard deviations for irradiated and dark control filtered estuary water for 20 experiments. Experiments were conducted using water from various stations between NAV and SPD from April 2005 to May 2008. Δ Light is the difference between concentrations in Light and T=0 with propagation of uncertainty, and Δ Dark is the difference between concentrations in Dark and T=0 with propagation of uncertainty.
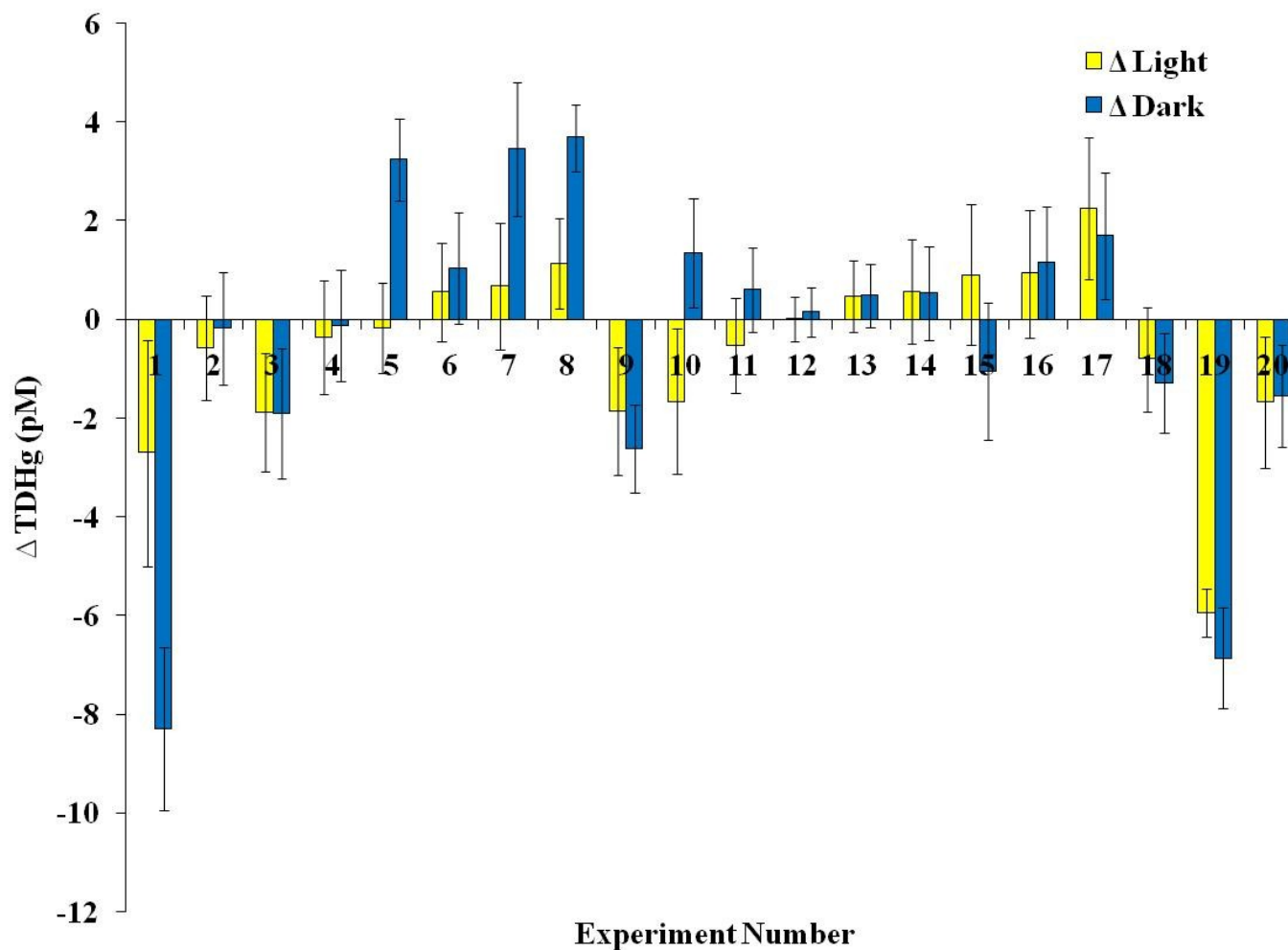
Figure 5.2 Changes in MeHg (pM) concentration and standard deviations for irradiated and dark control filtered estuary water for 7 experiments. Experiments were conducted using water from M61 and HB from April 2005 to May 2008. Δ Light is the difference between concentrations in Light and T=0 with propagation of uncertainty, and Δ Dark is the difference between concentrations in Dark and T=0 with propagation of uncertainty.
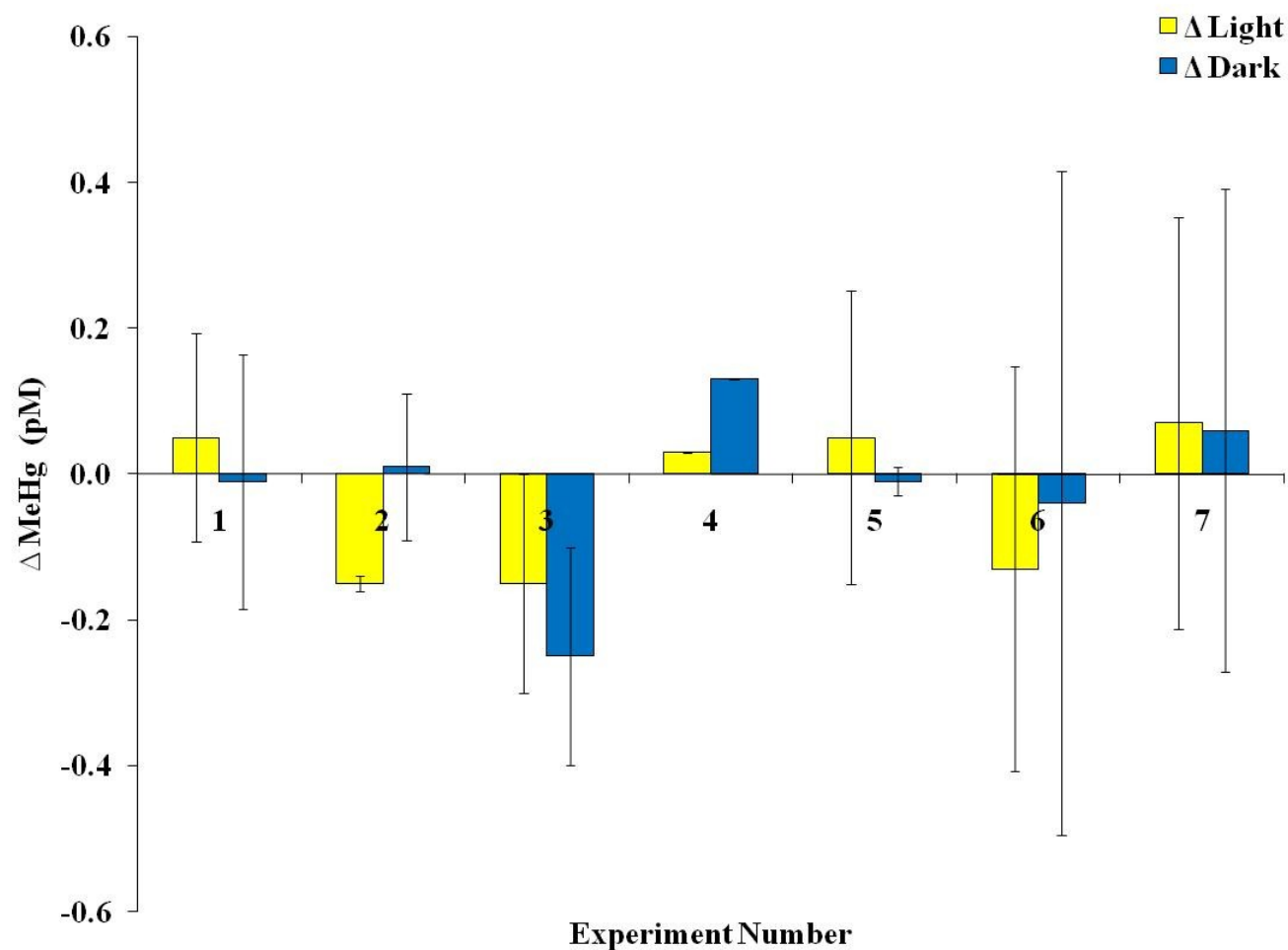
Figure 5.3. Changes in TDHg (pM) concentration and standard deviations for irradiated and dark control unfiltered estuary water for 20 experiments. Experiments were conducted using water from various stations between NAV and SPD from April 2005 to May 2008. Δ Light is the difference between concentrations in Light and T=0 with propagation of uncertainty, and Δ Dark is the difference between concentrations in Dark and T=0 with propagation of uncertainty.
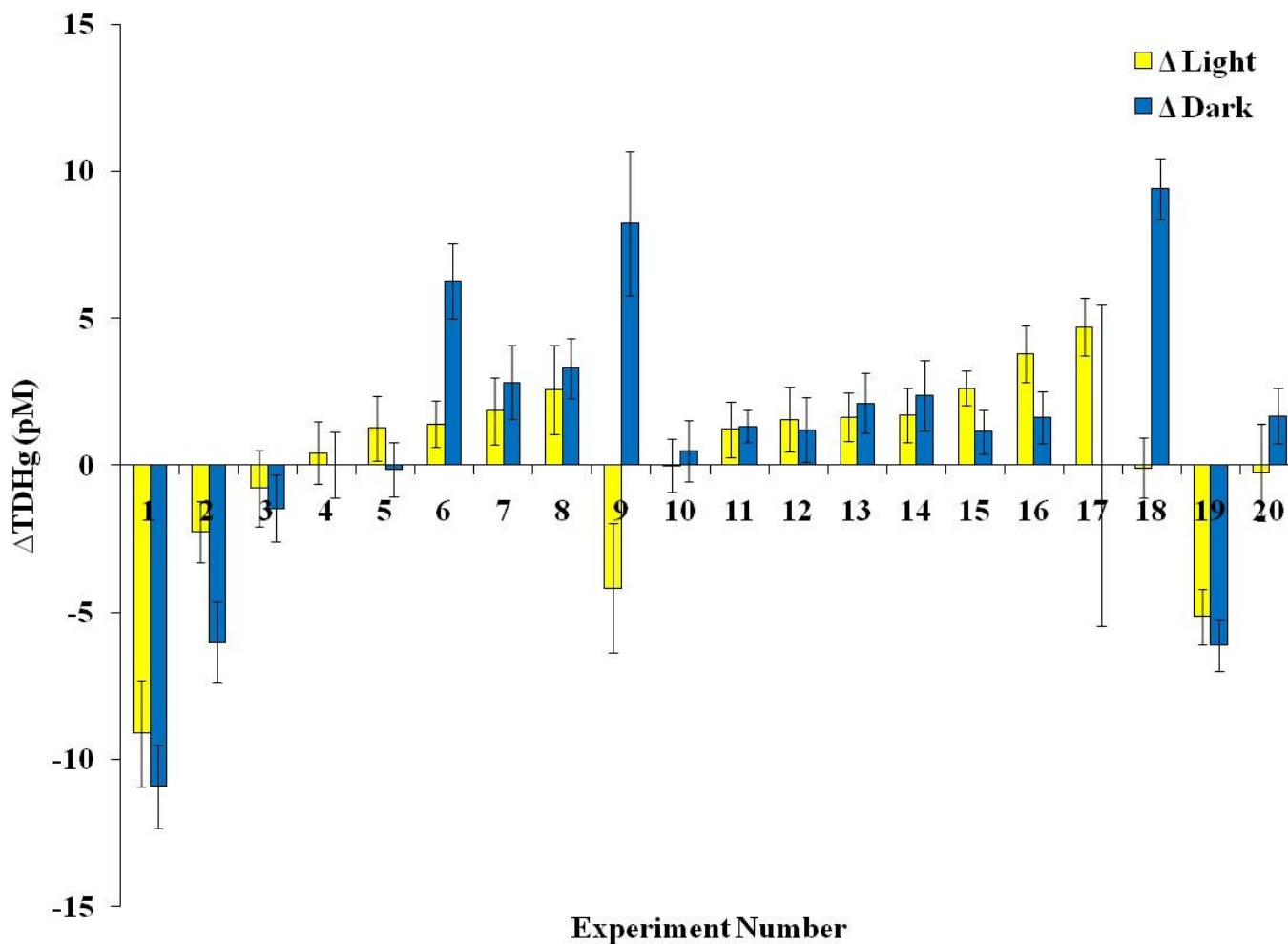
Figure 5.4. Changes in MeHg (pM) concentration and standard deviations for irradiated and dark control unfiltered estuary water for 7 experiments. Experiments were conducted using water from M61 and HB from April 2005 to May 2008. Δ Light is the difference between concentrations in Light and T=0 with propagation of uncertainty, and Δ Dark is the difference between concentrations in Dark and T=0 with propagation of uncertainty.
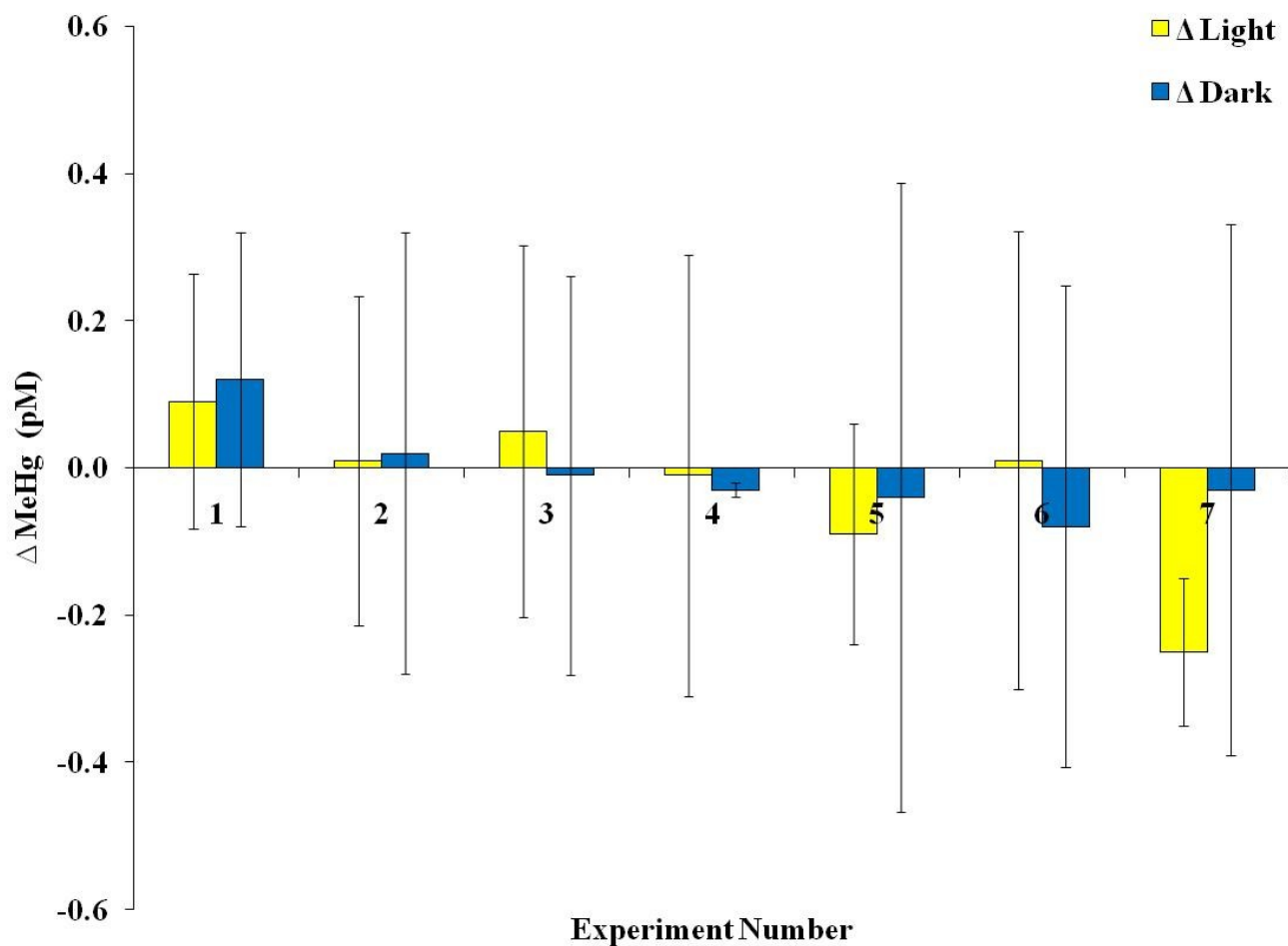
sediment from the corresponding station. This treatment was used to quantify the effect of irradiation of resuspended sediments on water column concentrations of TDHg and MeHg. Photolysis experiments were conducted ten times for TDHg and seven times for MeHg (Table 5.5). Experiments once again showed variable results after irradiation. TDHg concentrations decreased in seven experiments and increased in three (Figure 5.5). MeHg concentrations increased in two experiments decreased in four and did not change in one (Figure 5.6).

Photochemical Production of Dissolved Gaseous Hg

Photolysis experiments were conducted to quantify the amount of photochemically produced DGHg. These experiments were conducted at three stations in the estuary representing the freshwater, estuarine, and high salinity waters (Table 5.6).   Photochemical production of DGHg relative to dark controls was apparent in all six experiments. Production of DGHg ranged from 0.12 to 0.52 pM.

Photochemical Demethylation

Three experiments were conducted using surface water from station M61 to evaluate the photodemethylation rates in the Cape Fear River. Two of these experiments were conducted with 10 pM of added MeHg, and one with 3 pM added MeHg (Figures 5.7, 5.8 and 5.9). Demethylation occurred in both of the light treatments for all experiments and did not occur in the dark control treatment (Figures 5.7, 5.8 and 5.9). Demethylation rates (Table 5.7) were calculated using data from these three experiments using the following equations:

Figure 5.5. Changes in TDHg (pM) concentration and standard deviations for irradiated and dark control filtered estuary water containing 1.5 to 2.5 g of wet sediment for 10 experiments. Experiments were conducted using water from various stations between NAV and SPD from April 2005 to May 2008. Δ Light is the difference between concentrations in Light and T=0 with propagation of uncertainty, and Δ Dark is the difference between concentrations in Dark and T=0 with propagation of uncertainty.
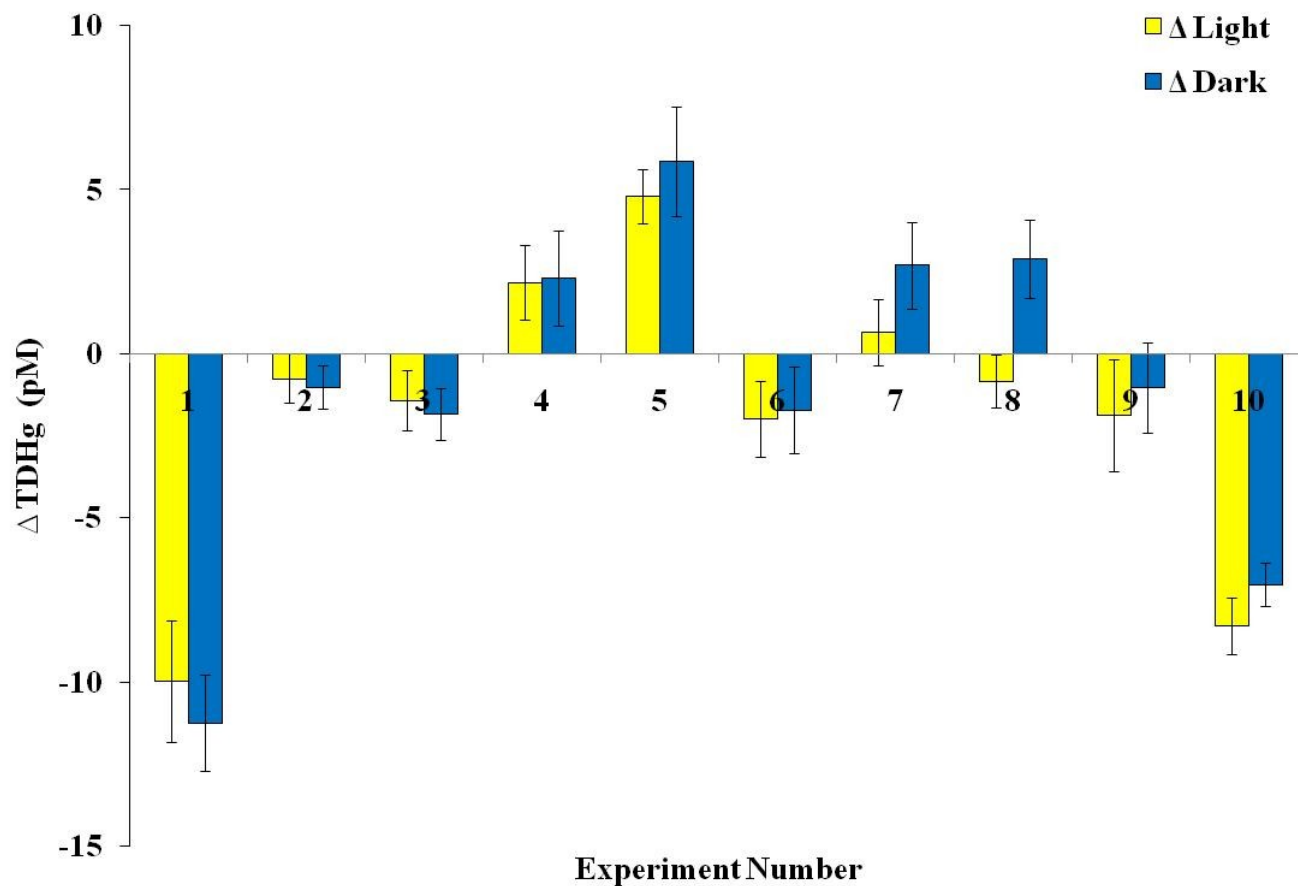
Figure 5.6. Changes in MeHg (pM) concentration and standard deviations for irradiated and dark control filtered estuary water containing 1.5 to 2.5 g of wet sediment for 7 experiments. Experiments were conducted using water from M61 and HB from April 2005 to May 2008. Δ Light is the difference between concentrations in Light and T=0 with propagation of uncertainty, and Δ Dark is the difference between concentrations in Dark and T=0 with propagation of uncertainty.
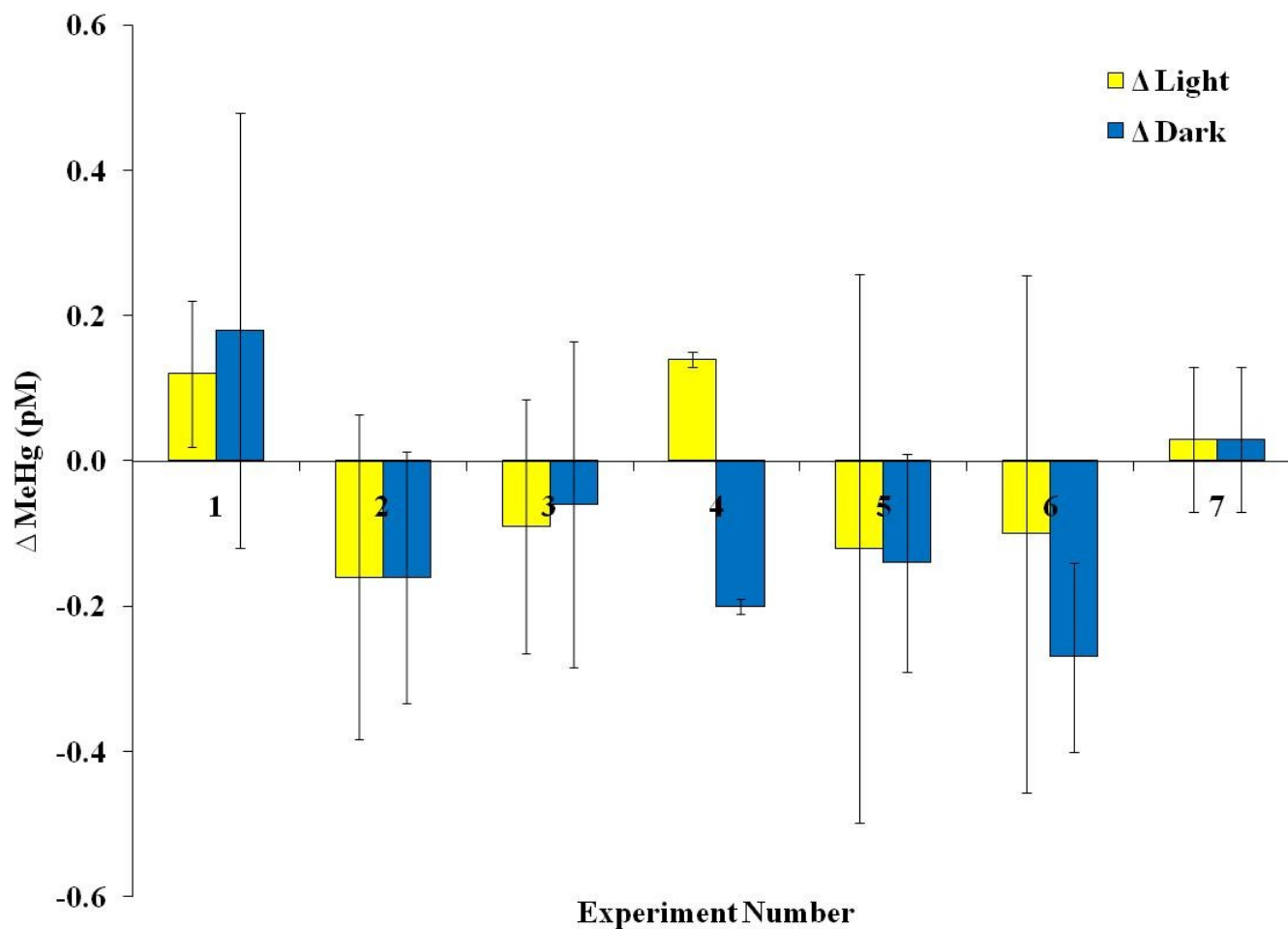
Table 5.6. Concentrations of DGHg (pM) in filtered estuary water from the Black River, Stations M18, M61 and HB initially (T=0), after 6 hours irradiation in the solar simulator and 6 hours in the dark. Δ Light is the difference between concentrations in Light and Dark. * denotes experiment conducted by Manley (2008). NA = not analyzed.

Date	Station	Treatment	T=0	Light	Dark	Δ Light
8/10/2007	Black River*	Unfiltered	0.11	0.63	-0.08	0.55
9/11/2007	Black River*	Unfiltered	-0.01	0.50	0.04	0.46
4/24/2008	M61	Unfiltered	0.41	NA	NA	NA
4/24/2008	M18	Unfiltered	0.17	0.48	0.21	0.27
4/24/2008	HB	Unfiltered	0.15	0.55	0.31	0.22
5/6/2008	M61	Unfiltered	0.52	NA	NA	NA
5/6/2008	M18	Unfiltered	0.23	0.35	0.10	0.15
5/6/2008	HB	Unfiltered	0.56	0.28	0.10	0.18

Figure 5.7. Concentration of MeHg(pM) in unfiltered and filtered water versus time (days) with M61surface water collected on May 8, 2008. Error bars represent standard deviation of replicate analysis.
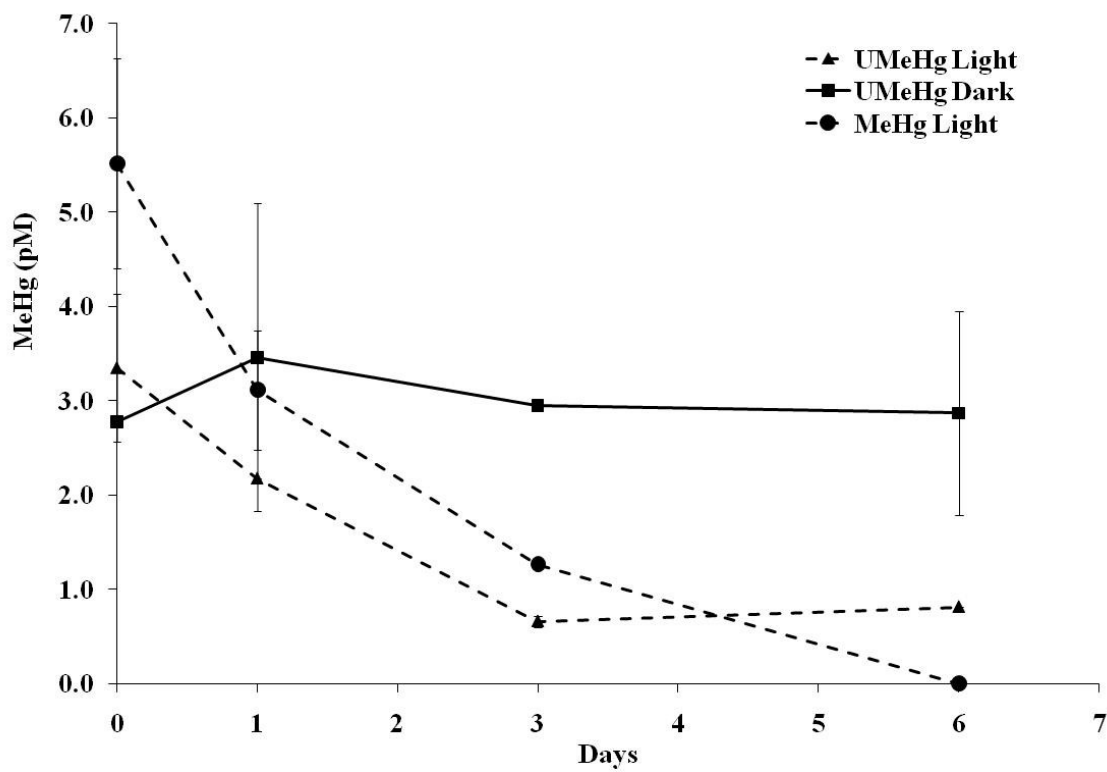
Figure 5.8. Concentration of MeHg(pM) in unfiltered and filtered water versus time (days) conducted with M61surface water collected on May 19, 2008. Error bars represent standard deviation of replicate analysis.
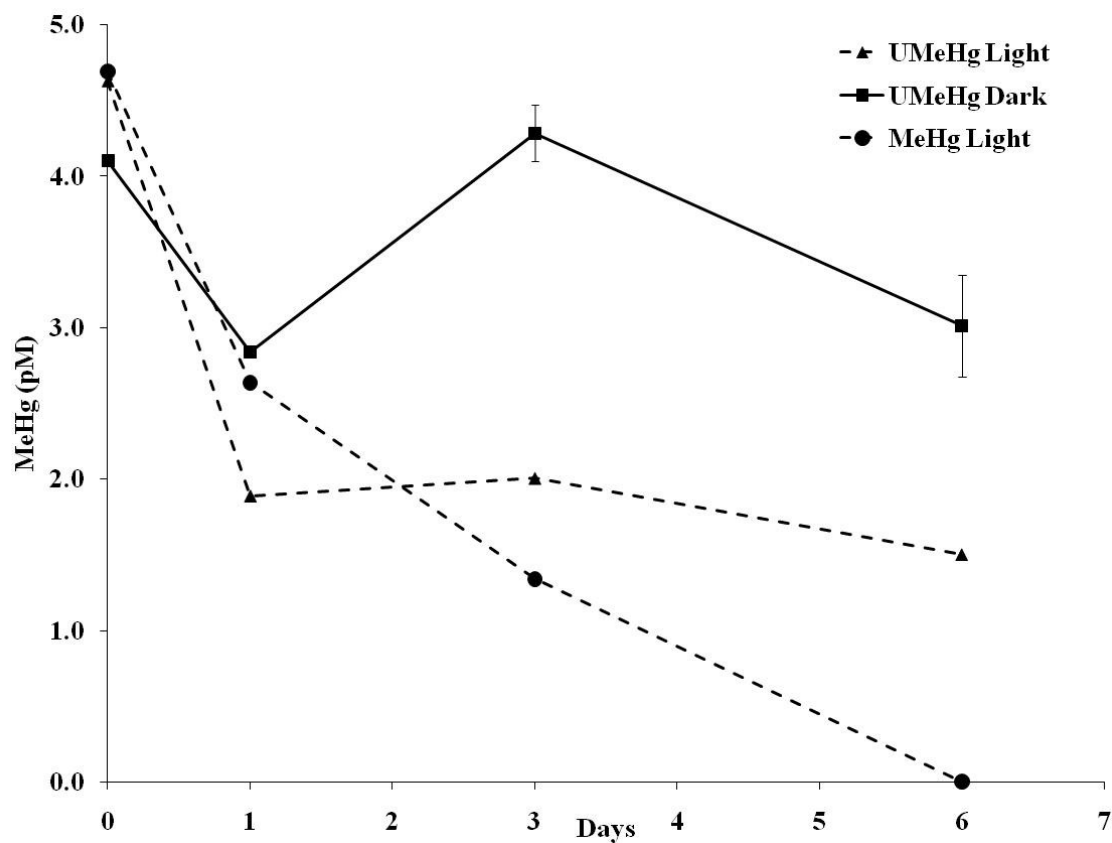
Figure 5.9. Concentration of MeHg(pM) in unfiltered and filtered water versus time (days) conducted with M61surface water collected on January 7, 2008. Error bars represent standard deviation of replicate analysis.
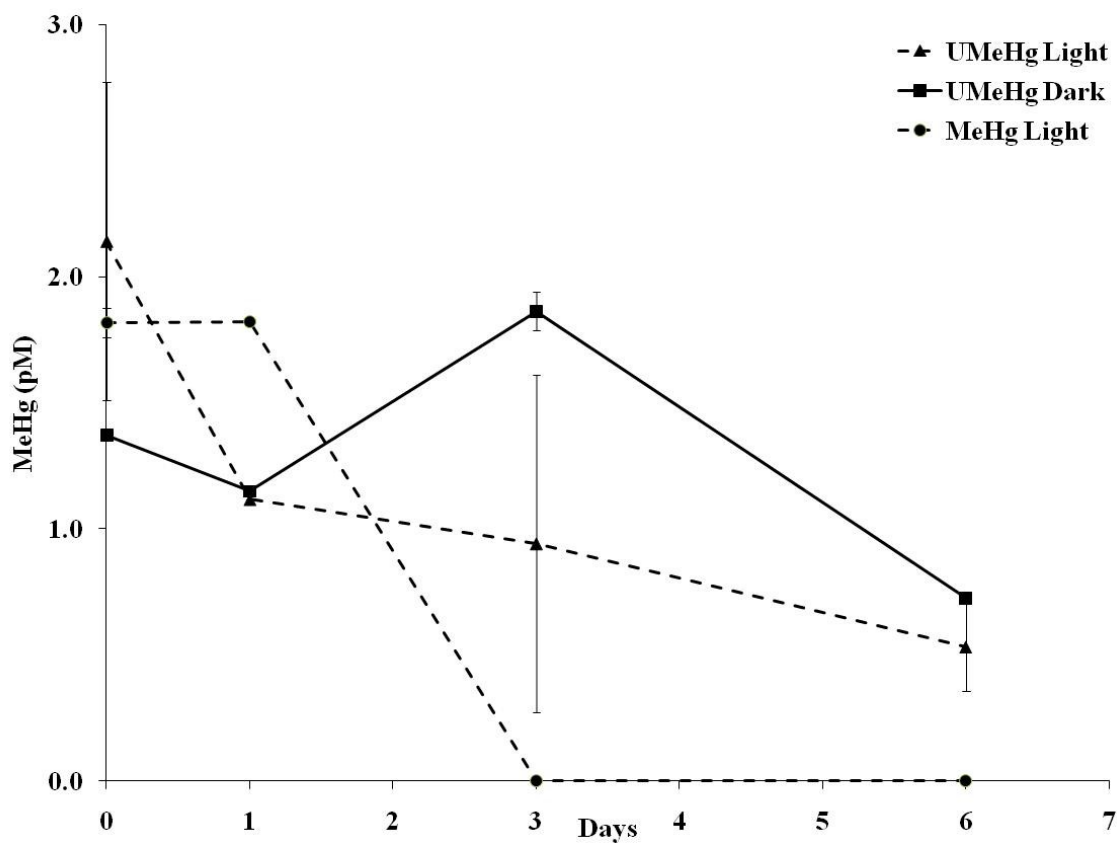
Table 5.7. Photodemethylation rates in pM d^{-1} and ng L^{-1} d^{-1} for two experiments conducted in May 2008 and one in January 2009 with surface waters collected from station M61. UMeHg denotes rate calculated in unfiltered M61 surface water and MeHg is the demethylation rate calculated in filtered M61 surface water.

	Experiment 1	pM d^{-1}	Experiment 2	pM d^{-1}	Experiment 3	pM d^{-1}
	UMeHg	MeHg	UMeHg	MeHg	UMeHg	MeHg
Day 0 to 3	0.90	1.42	0.87	1.12	0.40	0.60
Day 3 to 6	-0.05	0.42	0.17	0.45	0.14	0.00
	Experiment 1	ng L^{-1} d^{-1}	Experiment 2	ng L^{-1} d^{-1}	Experiment 3	ng L^{-1} d^{-1}
	UMeHg	MeHg	UMeHg	MeHg	UMeHg	MeHg
Day 0 to 3	0.18	0.28	0.18	0.22	0.08	0.12
Day 3 to 6	-0.01	0.08	0.03	0.09	0.03	0.00

$$\frac{[Day\ 0\ (ng\ L^{-1})] - [Day\ 3\ (ng\ L^{-1})]}{3} = rate\ of\ demethylation\ ng\ L^{-1}d^{-1}$$

and

$$\frac{[Day\ 3\ (ng\ L^{-1})] - [Day\ 6\ (ng\ L^{-1})]}{3} = rate\ of\ demethylation\ ng\ L^{-1}d^{-1}$$

From day 0 to day 3 demethylation rates were consistent between the two experiments where estuary water was spiked with 10 pM MeHg. In experiment 1, the demethylation rate for UMeHg was 0.18 ng L^{-1} d^{-1}, and in experiment 2 it was 0.18 ng L^{-1} d^{-1}. For MeHg, demethylation rates were also similar between experiments 1 and 2, calculated as 0.28 and 0.22 ng L^{-1} d^{-1} respectively.

Demethylation rates calculated from days 3 to 6 were again consistent between the two experiments, although they were smaller than those found from days 0 to 3 (Table 5.7). Rates for UMeHg were -0.01 and 0.08 ng L^{-1} d^{-1} for experiments 1 and 2 respectively. MeHg demethylation rates for experiments 1 and 2 were 0.08 and 0.09 ng L^{-1} d^{-1} respectively.

Sampling of each treatment for initial concentrations of MeHg was performed within 5 minutes of spiking the sample. Initial measurements did not recover the 10 pM spiked into the sample, suggesting rapid demethylation may have occurred as additional MeHg was added. A third experiment conducted using water from M61 and only spiked with 3 pM MeHg. Demethylation rates from day 0 to day 3 were 0.08 and 0.12 ng L^{-1} d^{-1} for UMeHg and MeHg respectively. Rates from day 3 to day 6 were 0.03 ng L^{-1} d^{-1} for UMeHg and not measurable for MeHg.

DISCUSSION

Photochemical Transformations of Total and MeHg

Three treatments of estuary water were irradiated to assess the photo-induced changes and role of sediments on Hg speciation in the water column. The three treatments were: filtered estuary water to assess photochemical release of TDHg and MeHg from DOC, unfiltered estuary water to assess release of TDHg and MeHg from ambient particles and filtered estuary water with sediment to assess the photochemical release of TDHg and MeHg from sediments. Changes in water column concentrations of both TDHg and MeHg after irradiation were highly variable between experiments and treatments. These experiments suggest that the uptake and release of Hg and MeHg from ambient particles may be occurring simultaneously during irradiation experiments and will have a small net impact on the speciation of Hg in the water column.

Effect of Sediment Resuspension

In April 2005 the sediment concentration was 248 ng Hg/g dry sediment, and even with this high concentration, resuspension of these sediments did not increase water column concentrations of TDHg. In May 2008, two experiments were conducted; sediment concentrations of Hg (23 and 24 ng Hg/g dry sediment) were lower than those used in the April 2005 experiment. These experiments once again showed removal of TDHg from the water column possibly by particle scavenging. Water column concentrations of MeHg were shown to decrease in one experiment and not change in the other.

The effect of sediment resuspension has been examined in mesocosms in Baltimore Harbor (Kim et al., 2004; Kim et al., 2006) and in natural waters of Hudson

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River and Mugu Lagoon, CA (Heyes et al., 2004; Rothenberg et al., 2008). Each of these studies concluded that resuspension did not impact water column concentrations of Hg, although they did not look at photochemical effects. No desorption of MeHg or TDHg was observed during photolysis of resuspension events. It has been suggested that particle desorption processes are not substantially occurring (Kim et al., 2004). It appears that this is also true in the waters in the Cape Fear River, as our experiments show no net impact of sediment resuspension on water column concentrations of TDHg or MeHg.

Photochemical Production of Dissolved Gaseous Hg

Photochemical production of dissolved gaseous Hg (DGHg) has been extensively studied in fresh and saltwater (Table 5.8) (Amyot et al., 1994; Xiao et al., 1995; Amyot et al., 1997a; Costa and Liss, 1999). Six experiments were conducted in the Cape Fear River to assess reduction of Hg^{2+} to Hg^o, with subsequent possible evasion from surface waters. Experiments conducted at three stations in the Cape Fear River (Table 5.6) show production of DGHg . These results show that photoreduction of Hg^{2+} is occurring in the Cape Fear River and is a removal process for Hg in the estuary. Production of DGHg in the Cape Fear River falls within the range of production in other natural waters.

Photochemical Demethylation

Experiments suggest that abiotic photodemethylation can occur in the Cape Fear River. In experiment 1 (Figure 5.7), there was no change in MeHg concentrations in the dark treatment and MeHg concentrations decreased when exposed to light in the unfiltered and 0.2 μm filtered treatments. Similar results were found in experiment 2 (Figure 5.8), although the concentration of MeHg in the dark treatment was more variable over the course of the experiment. The decrease in the filtered treatment when exposed

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Table 5.8. Production of DGHg(pM) in natural waters after irradiation with sunlight.

Location	DGHg (pM)	Reference
Ranger Lake, PA	0.1 – 0.9	Amyot et al. (1994)
Mediterranean Basin	0.06 – 0.1	Lanzillotta et al. (2002)
Gulf of Mexico	0.12	Amyot et al. (1997a)
Florida Everglades	0.99 – 1.9	Krabbenhoft et al. (1998)
Cape Fear River, NC	0.15 – 0.55	Present Study

to light suggests that abiotic demethylation occurs in the water column. Demethylation rates in the filtered treatments were faster than those in the unfiltered treatments. Experiments conducted in Toolik Lake, an optically clear arctic lake, suggest that abiotic demethylation is primary pathway of demethylation in surface waters (Sellers et al., 1996; Hammerschmidt and Fitzgerald, 2006). Demethylation rates in the Cape Fear River were similar to those found in Toolik Lake that ranged from 0 to 2 ng L^{-1}.

Demethylation rates in the Cape Fear River were dependent on initial MeHg concentration (Figure 5.10). The dependence of rate on concentration explains why demethylation is not seen in ambient concentrations. Demethylation rates were also found to be first order with respect to initial MeHg concentration (Figure 5.11). First order demethylation rate was also observed in Toolik Lake (Hammerschmidt and Fitzgerald, 2006). The first order rate allows us to calculate the half life of MeHg as 1.4.

The surface water demethylation rate in the Cape Fear River is comparable to the demethylation rate found at ~2 m in Toolik Lake. Despite the large difference in optical clarity, the rate in the surface waters of the Cape Fear River is similar to that found at greater depths in Toolik Lake. The mechanism of photodemethylation can compete with bioaccumulation and potentially decrease the amount of MeHg that could be transferred into the food web (Hammerschmidt and Fitzgerald, 2006). This mechanism may provide a sink of MeHg, since after demethylation has occurred the photochemical process may continue providing a pathway for evasion of DGHg from surface waters to the atmosphere.

Figure 5.10. Photochemical decomposition rate (pM d^{-1}) versus initial MeHg
concentration (pM) calculated using data from three demethylation experiments
conducted using water from station M61 collected on May 8 and May 19, 2008 and
January 7, 2009.

$y = 0.21x + 0.11$
$R^2 = 0.83$
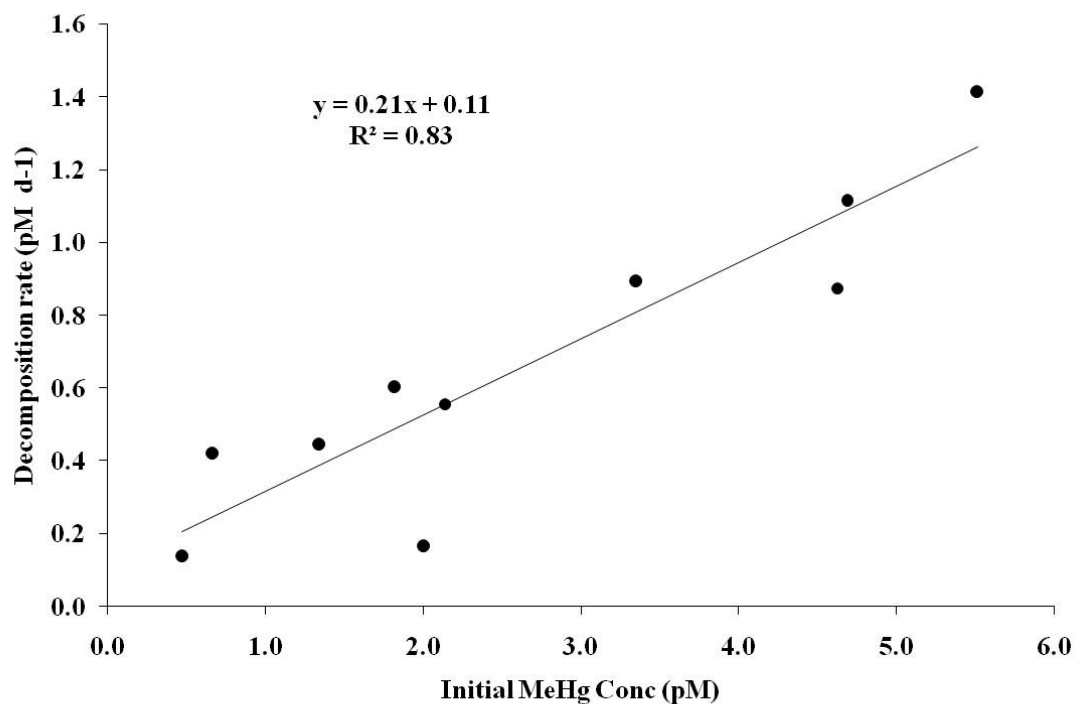
Figure 5.11. ln MeHg versus time (days) for photodemethylation experiment conducted on May 8, 2008.

$$y = -0.48x + 1.67$$

$$y = -0.55x + 1.26$$
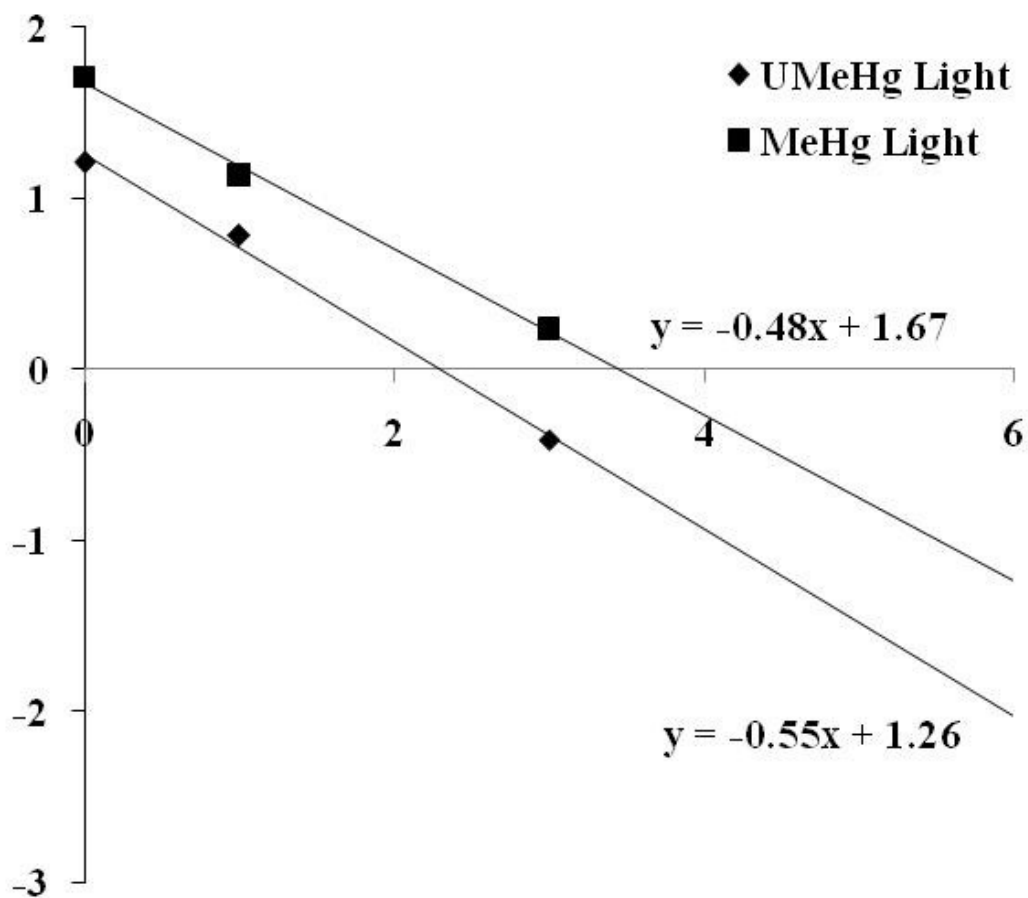
The photochemical demethylation pathway of

$$MeHg^+_{(aq)} \rightarrow Hg^{2+}_{(aq)} \rightarrow Hg^o_{(aq)} \rightarrow Hg^o_{(g)}$$
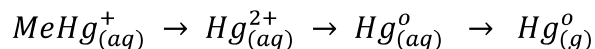
has been proposed (Sellers et al., 1996), ultimately leading to the evasion of DGHg from the water column. It is apparent from these experiments, that demethylation occurs even in the dark waters of the Cape Fear River.

SUMMARY

Photolysis experiments show that light-induced chemical transformations of Hg in the Cape Fear River are highly variable. Experiments indicate that there is no net change in water column concentrations of TDHg. Sediment resuspension experiments in the presence and absence of light does not affect water column concentrations of TDHg and MeHg. Photoproduction of DGHg occurs at numerous stations throughout the estuary, suggesting evasion as a sink for Hg in the estuary. The rate of DGHg production in the Cape Fear River is similar to other natural waters. Photodemethylation also occurs in the Cape Fear River, providing a pathway for removal of MeHg from the water column seen previously only in optically clear arctic waters.

Chapter 6 – Box Model and Mass Balance

The ultimate goal of this dissertation is to quantify the biogeochemical processes affecting the speciation and transport of Hg in the Cape Fear River estuary. Relevant processes include riverine input, waste water treatment effluent, phase transformations, photochemical transformations, atmospheric deposition, demethylation, biogenic uptake, benthic flux, evasion, *in situ* methylation and tidal exchange. Results from previous chapters along with additional data are used here to quantify two box models depicting mass balances for total Hg and MeHg in the Cape Fear River estuary.

Riverine Input

The Cape Fear River estuary receives 80% of water from the Cape Fear River, the Black River and the Northeast Cape Fear River. The Cape Fear River is a turbid Piedmont river, whereas the Black and Northeast Cape Fear are blackwater rivers that originate in the Coastal Plain. The average flow of these three rivers was compiled using USGS data (USGS, 2008) from January 1, 2004 to December 31, 2006 (Table 6.1). Average freshwater concentrations and standard deviations were calculated using Hg concentrations in waters with $S < 0.1$ from all sampling cruises. Using the average freshwater concentration data (Table 6.2) the number of moles contributed per year of dissolved, particulate and MeHg was calculated for each river using the following equation:

Mol y^{-1} Hg = freshwater concentration ± standard deviation (pmol L^{-1}) x

freshwater flowrate ($m^3 y^{-1}$) x 10^3 L m^{-3} x mol / 10^{12} pmol.

Table 6.1. Annual average flow rates (m^3/s) and standard deviations for the three rivers that supply freshwater to the Cape Fear River Estuary. Flow data from USGS from January 1, 2004 to December 31, 2006.

River	Gauge Location	2004	2005	2006	Average
Cape Fear River	Lock #1 NR Kelly, NC	129 ± 66	110 ± 84	128 ± 96	122 ± 81
Black River	Tomahawk, NC	19 ± 8	14 ± 7	25 ± 21	19 ± 14
NE Cape Fear River	Chinquapin, NC	19 ± 9	16 ± 10	32 ± 32	22 ± 21
Total Flow (m^3/s)					163 ± 85
Total Flow (m^3/y)					$5.1 \times 10^9 \pm 2.6 \times 10^9$

Table 6.2. Average concentrations (pM) and standard deviations of the various Hg species used in freshwater source calculations. Concentration data collected from July 2004 to September 2006.

River	n	TDHg	Hg$_{part}$	MeHg	MeHg$_{part}$
Cape Fear River	37	8 ± 6	14 ± 10	0.5 ± 0.4	0.6 ± 0.2
Black River	5	9 ± 6	11 ± 7	0.6 ± 0.6	0.5 ± 0.5
NE Cape Fear River	5	11 ± 8	15 ± 6	0.6 ± 0.4	0.5 ± 0.3

Inputs from each river were summed and standard deviations calculated by propagation of uncertainty to quantify the total freshwater input into the Cape Fear River Estuary for each Hg species. Riverine sources add 45 ± 15 mol TDHg y^{-1}, 70 ± 24 mol Hg$_{part}$ y^{-1}, 2.7 ± 1.1 mol MeHg y^{-1}, and 2.9 ± 0.6 mol MeHg$_{part}$ y^{-1}.

Wastewater Treatment Plant Effluent

There are two wastewater treatment plants that discharge effluent into the Cape Fear River estuary. The Northside Wastewater Treatment Plant discharges treated water in the upper estuary, while the Southside Wastewater Treatment Plant discharges into the middle estuary. Hg concentrations were determined on treated effluent at both plants in January 2008 (Table 6.3). The number of moles per year of the various Hg species entering the estuary from wastewater effluent was calculated as following equation:

$$Mol\ y^{-1}\ Hg = wastewater\ effluent\ concentration \pm standard\ deviation\ (pmol\ L^{-1})\ x$$
$$discharge\ rate\ (m^3y^{-1})\ x\ 10^3L\ m^{-3}\ x\ mol\ /\ 10^{12}pmol.$$

The two wastewater treatment plants in the Cape Fear River discharge 0.14 ± 0.001 mol TDHg y^{-1}, 0.10 ± 0.002 mol Hg$_{part}$ y^{-1}, 0.005 ± 7.2 x 10^{-5} mol MeHg y^{-1} and 0.002 ± 5.1 x 10^{-4} mol MeHg$_{part}$ y^{-1} respectively.

Atmospheric Deposition

Rainwater was collected laboratory from 76 rain events for total Hg and 30 events for MeHg, between September 2003 and September 2005 (Parler, 2005). Volume weighted average concentrations for TDHg, Hg$_{part}$ and MeHg are given in Table 6.4. Particulate Hg comprises approximately 30% off the total Hg found in wet deposition. MeHg$_{part}$ concentrations were not measured in

Table 6.3. Hg concentrations (pM) and standard deviation in discharge effluent from the Northside and Southside wastewater treatment plants, which discharge effluent into the Cape Fear River estuary.

	Flow	TDHg	Hg_{part}	MeHg	$MeHg_{part}$
Northside Plant	$9.5 \times 10^6 \pm 2.2 \times 10^5$	11 ± 3	6 ± 5	0.5 ± 0.05	0.25 ± 0.05
Southside Plant	$1.3 \times 10^6 \pm 7.1 \times 10^5$	22 ± 0.7	31 ± 3	0.6 ± 0.1	0.2 ± 0.07

Table 6.4. Volume weighted averages and standard deviations for rainwater collected from September 1, 2003 through September 30, 2005 (Parler 2005). Annual average rainfall amount is 1400 mm y^{-1}. *indicates estimated concentration of $MeHg_{part}$.

	Concentration (pM)
TDHg	35 ± 4
Hg_{part}	12 ± 1
MeHg	1.1 ± 0.1
$MeHg_{part}$ *	0.4 ± 0.3

rainwater, but assuming that MeHg$_{part}$ is similar to Hg$_{part}$, it is estimated to be approximately 1/3 of MeHg. The rainwater contribution of Hg to the estuary was determined as follows:

Mol y^{-1} Hg = volume weighted concentration ± standard deviation (pmol L^{-1}) x total depth of rainwater (m y^{-1}) x 10^{3}L m^{-3} x area of CFRE (1.1 x 10^{8} m^{2}) x mol / 10^{12}pmol.

This calculation includes rain deposited directly on the estuary surface, and does not include runoff through soils. Atmospheric wet deposition adds 6 ± 1 mol TDHg y^{-1}, 2 ± 0.2 mol Hg$_{part}$ y^{-1}, 0.17 ± 0.01 mol MeHg y^{-1} and an estimated 0.06 ± 0.003 mol MeHg$_{part}$ y^{-1}.

Benthic Flux

Sediments can be both a source and a sink for Hg in the water column (Chapter 4). Benthic flux measurements for the construction of this box model were calculated as both sources and sinks using the following equation:

mol Hg y^{-1} = flux of Hg (pmol m^{-2} d^{-1}) x 365 d y^{-1} x area of CFRE 1.1 x 10^{8} (m^{2}) x mol / 10^{12}pmol x 0.5.

The calculation is multiplied by 0.5 assuming the flux of Hg into or out of the sediments is occurring over half the estuary where organic rich fine grained sediments are found (Shank et al., 2004a). Benthic flux experiments (Tables 4.3 and 4.4) indicate that sediments act as both a source and sink for total Hg. Outward fluxes for sediments were 24 ± 17 mol TDHg y^{-1} and 58 ± 41 mol Hg$_{part}$ y^{-1}. When acting as a sink, sediments remove 35 ± 30 mol TDHg y^{-1} and 85± 74 mol Hg$_{part}$ y^{-1}. Sediments were never found to be a source of MeHg to the water column. As a sink, sediments removed 0.40 ± 0.26 mol MeHg y^{-1} and 0.34 ± 0.22 MeHg$_{part}$ mol y^{-1}.

Photochemical Transformations

Photolysis experiments conducted with Cape Fear Estuary water are discussed in Chapter 5. These experiments did not show a clear trend in affecting the water column concentrations of TDHg. Photochemical experiments demonstrate that MeHg is photochemically degraded and that the rate of degradation is directly dependent on the concentration of MeHg initially present.

Evasion

Photoproduction of DGHg was measured on three occasions using water from the Cape Fear River and is discussed in Chapter 5 (Table 5.6). The evasion of DGHg is a potential removal mechanism for Hg in the Cape Fear River estuary. The following equation from Rolfhus and Fitzgerald (2001) was used to estimate the DGHg flux from the Cape Fear River:

$$Hg^o \text{ flux to atmosphere} = k \, [Hg^o_{CFR} - Hg^o_{eq}],$$

where k = transfer velocity for Hg^o (cm h^{-1}) derived from the Wanninkhof model (Wanninkhof, 1992), Hg^o_{CFR} = dissolved gaseous Hg concentration in surface waters and Hg^o_{eq} = dissolved gaseous concentration in atmospheric equilibrium and is calculated using Henry's Law and the ideal gas equation (Rolfhus and Fitzgerald, 2001). The Wanninkhof model is widely accepted for determining wind-induced gas exchange fluxes (Rolfhus and Fitzgerald, 2001). The evasional flux for the Cape Fear River was estimated using the average Wannikhof k (2.014 m d^{-1}) and Hg^o_{eq} (0.06 pM) calculated for the Long Island Sound (Rolfhus and Fitzgerald, 2001). The estimated average evasional flux and standard deviation, based on 3 measurements, was calculated to be

442 ± 298 pmol m^{-2} d^{-1}, which was scaled over the area of the estuary using the following equation:

mol Hg y^{-1} = flux of Hg^o (pmol m^{-2} d^{-1}) x 365 d y^{-1} x area of CFRE (1.1 x 10^8 m^2) x mol /

$$10^{12} pmol.$$

Evasion of DGHg in the Cape Fear River estuary removes approximately 18 ± 12 mol y^{-1}. This source of elemental Hg to the atmosphere is small compared to emissions from cement plants where average Hg emissions in the US are 246 mol y^{-1}, and 80% of these emissions are as elemental Hg.

Photodemethylation

Photodemethylation experiments were conducted to evaluate this process as a removal mechanism for MeHg in the Cape Fear River estuary (Chapter 5). Rates of demethylation were calculated based on the loss of MeHg that occurred between days 0 and 3 of each experiment using the equation:

Rate of demethylation (pM d^{-1}) = [MeHg]$_0$ – [MeHg]$_3$ /d

where [MeHg]$_3$ = concentration of MeHg at day 3, [MeHg]$_0$ = initial MeHg concentration and d = number of days between sampling (Table 5.7). Ultraviolet sunlight only penetrates the top 2 cm of surface waters in the Cape Fear River (Whitehead and Kieber, unpublished data). Therefore calculated demethylation rates were scaled over the top 2 cm of the surface of the estuary.

mol Hg y^{-1} = rate of demethylation (pM d^{-1}) x 365 d y^{-1} x 10^3 L m^{-3} x 0.02m x area of

CFRE (m^2) x 1g /10^9 ng x mol / 201g.

The demethylation of Hg in the upper 2 cm of the surface waters of the Cape Fear River removes 0.9 ± 0.2 mol y^{-1}.

Ambient Particle Interactions and Sediment Resuspension

Particle and sediment interactions did not play a significant role in changing water column concentrations of TDHg or MeHg in the Cape Fear River estuary (Chapter 5). Resuspension experiments were performed in the dark, and did not show an impact on Hg transformations in the estuary.

Tidal Exchange

Tidal exchange between the Cape Fear River estuary and the Atlantic Ocean was estimated from the total volume of freshwater ($5.8 \times 10^9 \pm 2.6 \times 10^9 \, \text{m}^3\text{y}^{-1}$) (Table 6.1), calculated from the following equation:

$$Q_t = Q_1 + Q_2 + Q_3 + Q_4,$$

where Q_t = total outflow from estuary, Q_1 = discharge from Lock #1, Q_2 = discharge from Tomahawk, Q_3 = discharge from Chinquapin and Q_4 = estimated runoff (Geise et al., 1979). Lock #1, Tomahawk and Chinquapin are USGS gauges on the Cape Fear, Black and Northeast Cape Fear River respectively.

The amount of Hg leaving the estuary, using average Hg concentrations and standard deviations from the most seaward stations (M18 and M23), was calculated as follows:

Mol y^{-1} Hg = avg concentration at M18 and M23 (pmol L^{-1}) x freshwater flowrate (m^{3}y^{-1})

x 10^{3}L m^{-3} x mol / 10^{12}pmol.

The amount of Hg transported to the ocean is estimated to be 17 ± 7 mol TDHg y^{-1}, 19 ± 9 mol Hg_{part} y^{-1}, 1.5 ± 0.9 mol MeHg y^{-1}, and 1.2 ± 0.7 mol $\text{MeHg}_{\text{part}}$ y^{-1} respectively.

Biogenic Uptake

Many species of fish in the Cape Fear River are under consumption advisories due to high levels of MeHg in their tissues. Biogenic uptake of MeHg can be estimated by taking the difference between the sources and sinks of MeHg in the Cape Fear River Estuary. MeHg sources in the Cape Fear River include riverine input and atmospheric deposition totaling 5 ± 1 mol MeHg y^{-1}. Sinks for MeHg in the Cape Fear River estuary include sediment uptake (0.74 ± 0.34 mol MeHg y^{-1}), photodemethylation (0.9 ± 0.2 mol MeHg y^{-1}), and tidal exchange (2 ± 2 mol MeHg y^{-1}) for a total of 4 ± 2 mol MeHg y^{-1}. The difference between the sources and sinks allow us to estimate biogenic uptake of 1 ± 2 mol MeHg y^{-1}.

Box Models

Box models were constructed to encompass the area of the estuary from stations NAV to M61(Figure 6.1, 6.2, 6.3,6.4, and Table 6.5). Important sources of total Hg to the Cape Fear River estuary are riverine, atmospheric, and sediment inputs. For MeHg important sources are riverine input and estimated *in situ* methylation. The largest sink for total Hg was burial by sediments and assumed biogenic uptake for MeHg. In the Cape Fear River estuary, sediments can acts as both a source and a sink for water column Hg. Local wastewater treatment plants were not a significant source of either total Hg or MeHg to the Cape Fear River estuary. Data in Table 6.5 suggest that despite considerable uncertainty, ~20 mol Hg y^{-1} may be exported out of the estuary.

Figure 6.1. Estuarine box model for dissolved Hg in the Cape Fear River estuary. Fluxes are given in mol y^{-1} ± standard deviations. [1] indicates evasion calculated using an unfiltered sample and contains both dissolved and particulate Hg.
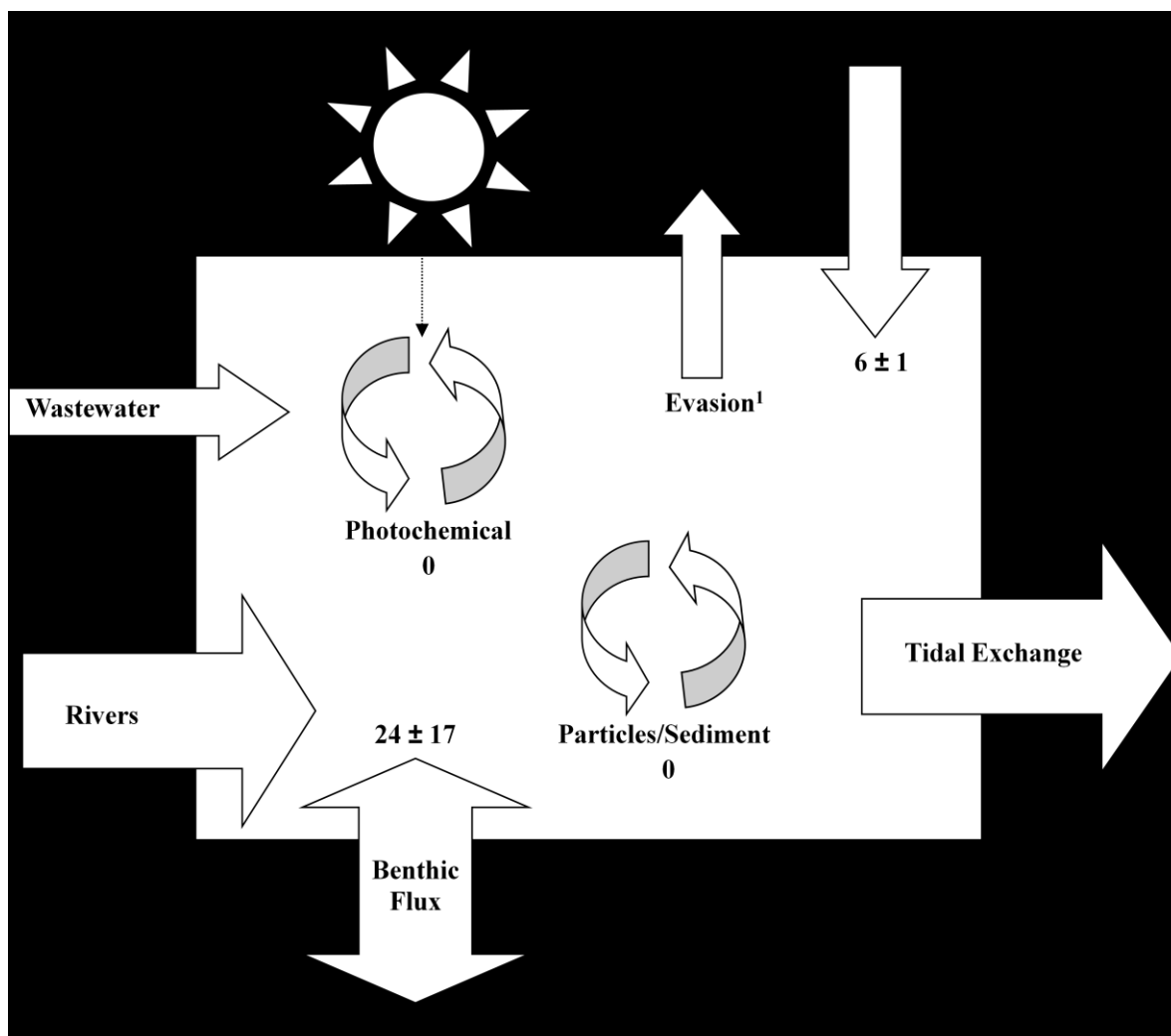
Figure 6.2. Estuarine box model for particulate Hg in the Cape Fear River estuary. Fluxes are given in mol y^{-1} ± standard deviations. [1] indicates evasion calculated using an unfiltered sample and contains both dissolved and particulate Hg.
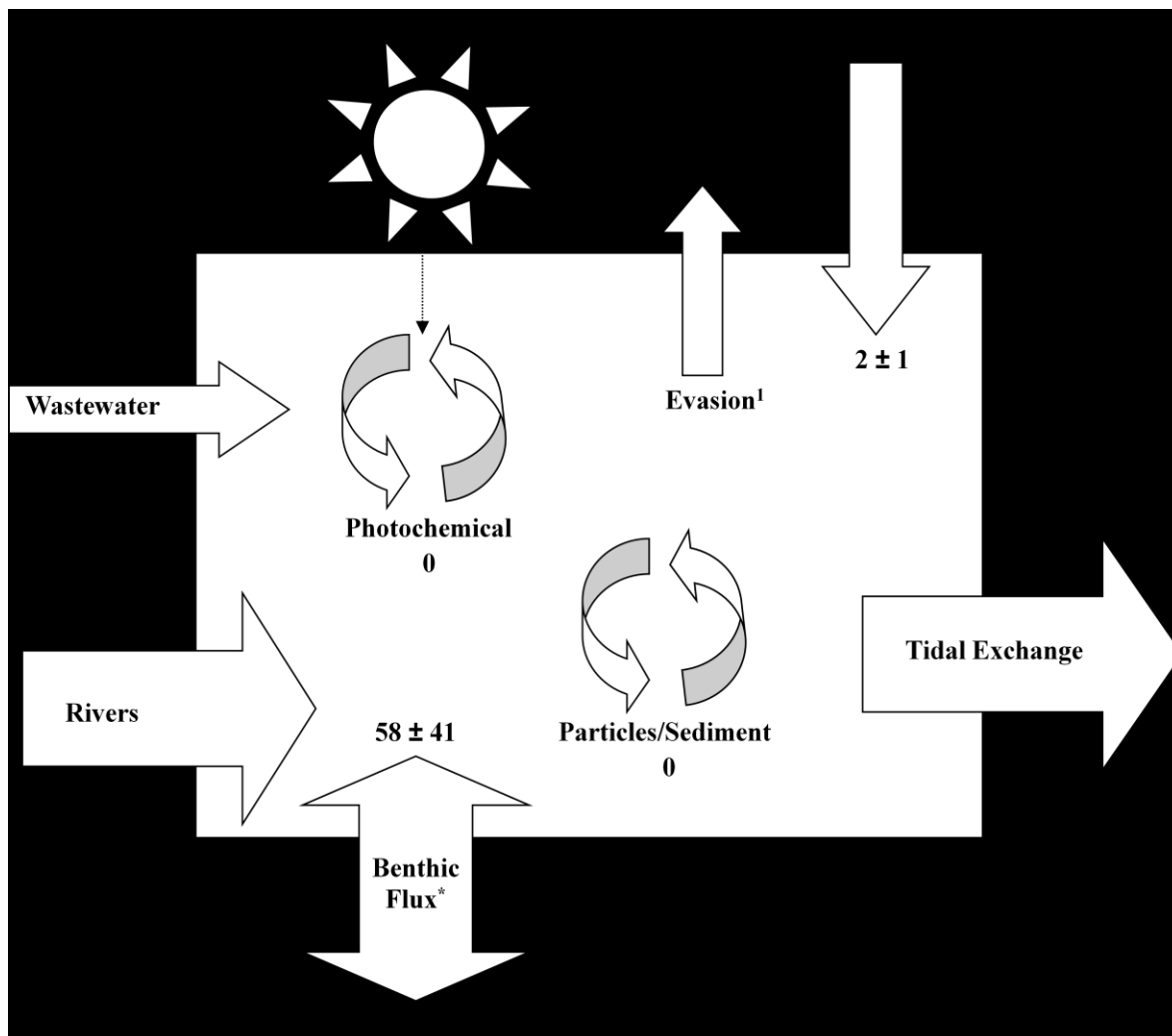
Figure 6.3. Estuarine box model for total (dissolved + particulate) Hg in the Cape Fear River estuary. Fluxes are given in mol y^{-1} ± standard deviations.
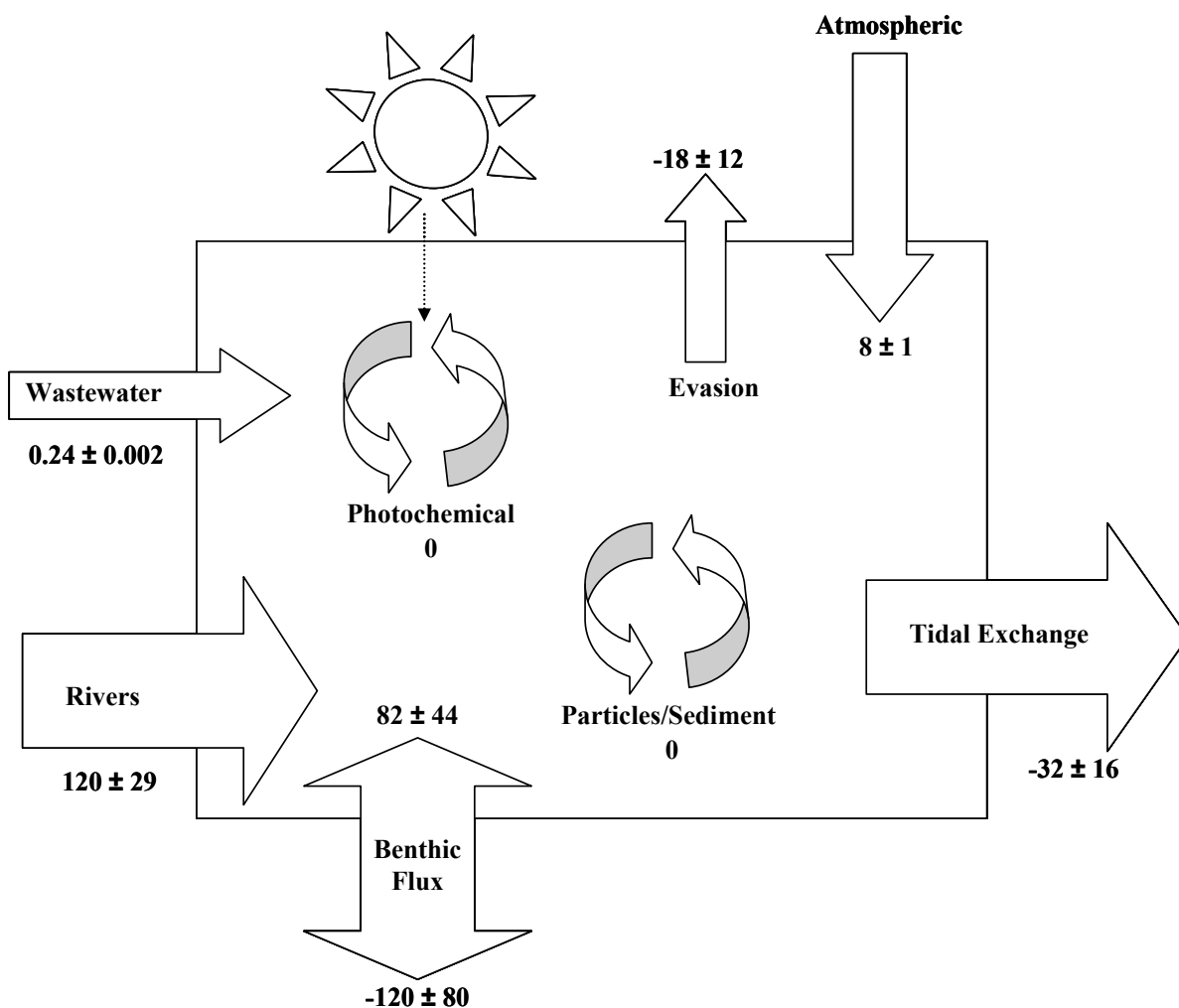
Figure 6.4. Estuarine box model for MeHg in the Cape Fear River estuary. Fluxes are given in mol y^{-1} ± standard deviations.
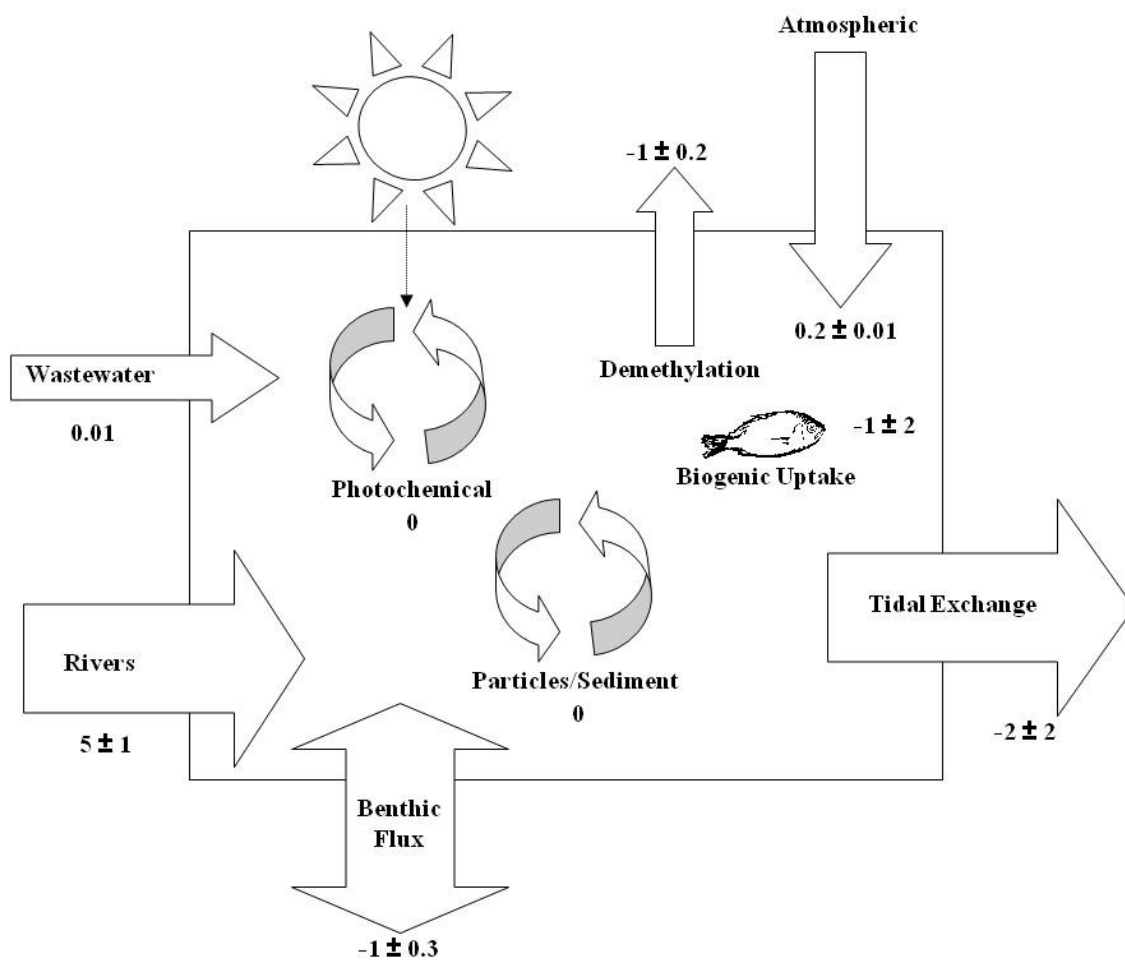
Table 6.5. Sources and sinks of dissolved, particulate and MeHg (mol y^{-1} ± standard deviations) in the Cape Fear River estuary. * indicates estimated fluxes. [1] indicates evasion entered in particulate Hg column.

Sources	Dissolved Hg	Particulate Hg	MeHg
Riverine	44 ± 14	69 ± 25	5 ± 1
Atmospheric	6 ± 1	2 ± 0.2	0.2 ± 0.01
Wastewater Treatment Plant	0.14 ± 0.001	0.1 ± 0.002	0.01 ± 5.2 x 10^{-4}
Benthic Flux	24 ± 17	58 ± 41*	0
Total Sources	74 ± 22	129 ± 48	5 ± 1
Sum of all Hg species	208 ± 53		

Sinks	Dissolved Hg	Particulate Hg	MeHg
Benthic Flux	35 ± 30	85 ± 74*	1 ± 0.3
Evasion*	[1]	18 ± 12*	NA
Demethylation	NA	NA	1 ± 0.2
Tidal Exchange	17 ± 7	19 ± 9	2 ± 2
Biogenic Uptake*	NA	NA	1 ± 2
Total Sinks	52 ± 31	122 ± 76	5 ± 2
Sum of all Hg species	170 ± 82		

DISCUSSION

A comparison of mass balance models for the Cape Fear River and four other estuaries in the United States are presented in Tables 6.6 and 6.7. In order to compare the various estuaries, sources and sinks for total Hg and MeHg are presented as percentages in Table 6.8 and 6.9. Comparison of the Cape Fear River to other estuaries will elucidate how impacted the CFRE is by Hg. The estuaries used for comparison are Long Island Sound (LIS), New York New Jersey Harbor (NYH), San Francisco Bay (SFB) and Chesapeake Bay (CB). These estuaries range in size from 110 km^2 (CFRE) to 3250 km^2 (LIS). Although there is a large range in size between these estuaries, in the LIS, NYH, SFB and CB, Hg loadings are dominated by riverine and atmospheric inputs and internal production is an important source of MeHg (Fitzgerald et al., 2007).

Mass balances for these estuaries have identified the major processes controlling Hg cycling, including evasion, methylation, bioaccumulation, photodecomposition and net ocean export. The importance of atmospheric deposition is variable between the five estuaries. Input of Hg from wet deposition in the Cape Fear River estuary (CFRE) is similar to that found in the NY/NJ Harbor (NYH) and San Francisco Bay (SFB). Atmospheric deposition is relatively larger in Long Island Sound (LIS) and Chesapeake Bay (CB), perhaps due to the presence of large urban areas nearby. Inputs in CB are higher because they include wet and dry deposition concentrations (Mason et al., 1999). Atmospheric flux of Hg was estimated from the Hg Deposition Network in NYH, and was measured as wet deposition in LIS and SFB. The input for LIS is larger than that of the CFRE, even though wet deposition in both areas measured ~40 pM Hg. This may be due to the larger area of the LIS (3250 km^2) versus the CFRE (110 km^2).

Table 6.6. Total Hg Mass Balance Models for Five Estuaries in the United States. Fluxes are in mol y^{-1} for each process. NA = not analyzed.

	NY/NJ Harbor Balcolm et al., 2007	San Francisco Bay MacLeod et al., 2005	Long Island Sound Balcolm et al., 2004 Hammerschmidt et al., 2004	Chesapeake Bay Mason et al., 1994	Cape Fear River Present Study
Sources					
Atmospheric	27	20	130	1300	8
Riverine	2270	1208	970	2125	113
WWTP	140	18	60	NA	0.24
Sediment flux	NA	NA	NA	NA	82
Total Sources	2437	1246	1160	3425	203
Sinks					
Bioaccumulation	NA	NA	NA	50	NA
Evasion	60	3	400	580	18
Tidal Exchange	1560	513	80	1085	36
Burial	820	732	680	1890	NA
Sediment Flux					120
Total Sinks	2440	1248	1160	3605	174

Table 6.7. MeHg mass balance models for five estuaries in the United States. Fluxes are in mol y^{-1} for each process. NA = not analyzed.

	NY/NJ Harbor	San Francisco Bay	Long Island Sound	Chesapeake Bay	Cape Fear River
	Balcolm et al., 2007	MacLeod et al., 2005	Balcolm et al., 2004 Hammerschmidt et al., 2004	Mason et al., 1994	Present Study
Sources					
Atmospheric	0.5	NA	3.5	6.5	0.16
Riverine	21	1	22.5	27.6	5
WWTP	3	NA	1.5	NA	0.01
In situ methylation	8	2	55	63.2	0
Total Sources	32.5	3	82.5	97.3	5.2
Sinks					
Bioaccumulation	12.5	NA	50	50	1
Tidal Exchange	14	2	1.5	37.8	2
Burial	4	1	5.2	9.5	1
Demethylation	2	NA	27	NA	1
Total Sinks	32.5	3	83.7	97.3	5

Table 6.8. Percentage of total sources and sinks for total Hg in Five Estuaries in the United States showing their relative importance.

	NY/NJ Harbor Balcolm et al., 2007	San Francisco Bay MacLeod et al., 2005	Long Island Sound Balcolm et al., 2004 Hammerschmidt et al., 2004	Chesapeake Bay Mason et al., 1994	Cape Fear River Present Study
Sources					
Atmospheric	1%	2%	11%	38%	4%
Riverine	93%	97%	84%	62%	54%
WWTP	6%	1%	5%	0%	0.1%
Sediment flux	NA	NA	NA	NA	40%
Sinks					
Bioaccumulation	NA	NA	NA	1%	NA
Evasion	2%	0%	34%	16%	10%
Tidal Exchange	64%	41%	7%	30%	20%
Burial	34%	59%	59%	52%	69%

Table 6.9. Percentage of total sources and sinks for MeHg in Five Estuaries in the United States showing their relative importance.

	NY/NJ Harbor	San Francisco Bay	Long Island Sound	Chesapeake Bay	Cape Fear River
	Balcolm et al., 2007	MacLeod et al., 2005	Balcolm et al., 2004 Hammerschmidt et al., 2004	Mason et al., 1994	Present Study
Sources					
Atmospheric	2%	0%	4%	7%	2%
Riverine	65%	33%	27%	28%	54%
WWTP	9%	0%	2%	0%	0.1%
In situ methylation	25%	67%	67%	65%	44%
Sinks					
Bioaccumulation	38%	NA	60%	51%	56%
Tidal Exchange	43%	67%	2%	39%	22%
Burial	12%	33%	6%	10%	11%
Demethylation	6%	NA	32%	NA	11%

Riverine flow is the dominant input for all five estuaries. Freshwater concentrations of Hg used in calculating the riverine input were similar among the 5 estuaries. The other estuaries used as comparison are larger in size and have more riverine inputs than found in the CFRE, influencing the magnitude of these sources.

Hg input from wastewater treatment plants is not large in the CFRE relative to SFB and CB. Wastewater treatment plants are of importance in NYH and LIS. In the CFRE there are two treatment plants that discharge into the estuary. In NYH there are 14 plants and in LIS 14 major plants and 70 smaller ones that discharge into the estuary. The larger number of plants in NYH and LIS may explain the greater influence on these systems relative to that of the CFRE.

Evasion of DGHg was not measured in all estuaries. Gas exchange was estimated in CB and SFB. In NYH, LIS and CFRE was estimated using DGHg measurements and constants using the model from Rolfhus and Fitzgerald (2001). Evasion of DGHg is an important sink in LIS, CB and CFRE. *In situ* methylation was not measured in all estuaries, but is estimated to be 2% of the total Hg inputs to each system based on the measurements made by Mason (Mason et al., 1999) in Chesapeake Bay.

Burial of Hg was calculated differently in each estuary. Burial was calculated in NYH as the difference between the sources and sinks in the mass balance for total Hg . MeHg burial was estimated as 0.5% of the total Hg burial found by the difference between sources and sinks (Balcom et al., 2008; Hammerschmidt and Fitzgerald, 2008). In LIS and CB it was calculated using sedimentation rates. Burial is an important sink in all the estuaries; the variability in importance may have to do with the calculation method.

Demethylation was estimated in LIS and NYH using rates from Hammerschmidt and Fitzgerald (2006). In the CFRE, experiments were conducted using ambient water to calculate demethylation rates. Rates used for demethylation in LIS and NYH were calculated for an optically clear lake. The calculation for LIS may be overestimated due to the calculation using the rate from an optically clear lake.

The common findings in all five estuaries are that the primary sources of Hg to these systems are riverine sources and atmospheric deposition. Wastewater treatment plants are not a significant local source to the Cape Fear River for either total Hg or MeHg, and are similar to inputs found in San Francisco Bay and Chesapeake Bay. Sediment flux of total Hg is an important source in the Cape Fear River, although intermittent, at times accounting for almost half of the input to the estuary. Atmospheric sources are similar to those found in NYNJ Harbor and San Francisco Bay, while they are a larger source in Long Island Sound and Chesapeake Bay due to incorporation of wet and dry deposition into the flux calculation.

The most important sinks of total Hg in the five estuaries are burial, and bioaccumulation of MeHg. Tidal exchange accounts for approximately 20% of Hg loss from the Cape Fear River estuary for both total Hg and MeHg. Evasion and demethylation are also sinks for total Hg and MeHg. Although the magnitudes of Hg entering the various estuaries are highly variable, it is apparent that the percentages of sources and sinks are comparable with one another. Each system will have its own local impacts that may affect these mass balances, but the important sources across these systems appear to be riverine, atmospheric input and *in situ* methylation. In NYH and LIS, there are a large number of wastewater treatment plants which have a larger impact on the sources of Hg in these systems. The important sinks for total Hg and MeHg are benthic flux, tidal exchange and

bioaccumulation. Evasion and demethylation were not measured in all systems and so it is difficult assess the importance of these sinks among the different systems. In the CFRE, there is possibility of Hg export the coastal ocean. Total Hg inputs are 208 mol y^{-1} and exports are 174 mol y^{-1}. Given the uncertainty of benthic flux measurements and lack of burial for the CFRE, approximately 20 mol Hg y^{-1} may be exported to the coastal waters of southeastern North Carolina.

CONCLUSIONS

This dissertation provides a detailed and comprehensive study on Hg speciation and distribution in the Cape Fear River estuary. In the Cape Fear River, Hg is found in concentrations that are comparable to other minimally to moderately impacted estuaries. Parameters controlling Hg are DOC for TDHg and MeHg and suspended particle matter for Hg_{part}. River flow also plays an important role in controlling the concentrations and distributions of the various Hg species in the estuary. Benthic flux experiments indicate that the sediments can act as both a source and sink of total Hg to the waters of the Cape Fear River. These experiments also demonstrate sediments are a sink for MeHg, rather than a source as observed in the Chesapeake Bay.

Photolysis of Cape Fear River waters does not have a large impact on the speciation of dissolved Hg in the water column. These experiments also show that photolysis of ambient particles and resuspended sediment does not impact water column concentrations of Hg. Although photolysis does not impact water column concentrations of TDHg, irradiation of surface waters can produce DGHg and promote demethylation removing Hg from the estuary.

Data collected throughout the duration of this research were used to establish the sources and sinks of Hg and MeHg to the Cape Fear River estuary. Riverine inputs are the primary sources of both total Hg and MeHg, while sediment fluxes are source and sink for total Hg. Tidal exchange removes approximately 20% of both total and MeHg, indicating that most of Hg is trapped within the estuary but there Hg is being exported to the coastal ocean. The magnitude of sources and sinks for total Hg and MeHg in the Cape Fear River estuary are comparable to other moderately impacted estuaries.

REFERENCES

Amyot, M., Auclair, J.C. and Poissant, L., 2001. In situ temporal resolution analysis of elemental mercury in natural waters. Analytica Chimica Acta, 447: 153-159.

Amyot, M., Gill, G.A. and Morel, F.M.M., 1997a. Production and loss of dissolved gaseous mercury in coastal seawater. Environmental Science and Technology, 31: 3606-3611.

Amyot, M., Lean, D.R.S. and Mierle, G., 1997b. Photochemical Formation of Volatile Mercury in High Arctic Lakes. Environmental Toxicology and Chemistry, 16(10): 2054-2063.

Amyot, M., Mierle, G., Lean, D.R.S. and McQueen, D.J., 1994. Sunlight-Induced Formation of Dissolved Gaseous Mercury in Lake Waters. Environmental Science and Technology, 28(2366-2371).

Amyot, M., Mierle, G., Lean, D.R.S. and McQueen, D.J., 1997c. Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes. Geochimica et Cosmochimica Acta, 61(5): 975-987.

Avery, G.B., Willey, J.D., Kieber, R.J., Shank, G.C. and Whitehead, R.F., 2003. Flux and bioavailability of Cape Fear River and rainwater dissolved organic carbon to Long Bay, southeastern United States. Global Biogeochemical Cycles, 17(2).

Baeyens, W. et al., 2003. Bioconcentration and Biomagnification of Mercury and Methylmercury in North Sea and Scheldt Estuary Fish. Archives of Environmental Contamination and Toxicology, 45(4): 498-508.

Baeyens, W., Meuleman, C., Muhaya, B. and Leermakers, M., 1998. Behaviour and speciation of mercury in the Scheldt estuary (water, sediments and benthic organisms). Hydrobiologia, 366: 63-79.

Balcom, P.H., Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H. and O'Connor, J.S., 2008. Seasonal distributions and cycling of mercury and methylmercury in the waters of New York/New Jersey Harbor Estuary. Marine Chemistry, 109(1-2): 1-17.

Benoit, G. et al., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. Marine Chemistry, 45(4): 307-336.

Benoit, J.M., Gilmour, C.C., Mason, R. and Heyes, A., 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environ. Sci. Technol., 33: 951-957.

Benoit, J.M., Gilmour, C.C., Mason, R.P., Riedel, G.S. and Riedel, G.F., 1998. Behavior of mercury in the Patuxent River Estuary. Biogeochemistry, 40: 249-265.

Bloom, N. and von der Geest, E., 1995. Matrix Modification to Improve Recovery of CH3Hg from Clear Waters using the Acid/Chloride Distillation Procedure. Water Air and Soil Pollution, 80: 1319.

Bloom, N.S. and Crecelius, E.A., 1983. Determination of Mercury Seawater at Sub-Nanogram Per Liter Levels. Marine Chemistry, 14: 49-59.

Bloom, N.S. et al., 1999. Speciation and Cycling of Mercury in Lavaca Bay, Texas, Sediments. Environ. Sci. Technol., 33(1): 7-13.

Bothner, M.H., Buchholtz ten Brink, M. and Manheim, F.T., 1998. Metal Concentrations in Surface Sediments of Boston Harbor- Changes with Time. 45(2): 127-155.

BS7755, I.a., 1995. ISO 10694 and BS7755, Determination of organic and total carbon after dry combustion, British Standard Methods of Tests for Soils for Civil Engineering Purposes: Part 3. British Standard Institution, London.

Burdige, D.J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. Earth-Science Reviews, 35: 249–284.

Choe, K.Y., Gill, G.A. and Lehman, R., 2003. Distribution of particulate, colloidal, and dissolved mercury in San Francisco Bay estuary. 1. Total mercury. Limnology and Oceanography, 48(4): 1535-1546.

Choe, K.Y. et al., 2004. Sediment-water exchange of total mercury and monomethyl mercury in the San Francisco Bay-Delta. Limnology and Oceanography, 49(5): 1512-1527.

Choi, S.C. and Bartha, R., 1994. Environmental Factors Affecting Mercury Methylation in Estuarine Sediments. 53: 805-812.

Compeau, G.C. and Bartha, R., 1985. Sulfate-Reducing Bacteria: Principal Methylators of Mercury in Anoxic Estuarine Sediment. Applied and Environmental Microbiology, 50(2): 498-502.

Conaway, C.H., Squire, S., Mason, R.P. and Flegal, A.R., 2003. Mercury speciation in the San Francisco Bay estuary. Marine Chemistry, 80(2-3): 199-225.

Coquery, M., Cossa, D. and Sanjuan, J., 1997. Speciation and sorption of mercury in two macro-tidal estuaries. Marine Chemistry, 58(1-2): 213-227.

Cossa, D., Gobeil, C. and Courau, P., 1988. Dissolved mercury behaviour in the Saint Lawrence estuary. Estuarine, Coastal and Shelf Science, 26(2): 227-230.

Costa, M. and Liss, P.S., 1999. Photoreduction of mecury in seawater and its possible implications for Hg^0 air sea fluxes. Marine Chemistry, 68: 87-95.

Costa, M. and Liss, P.S., 2000. Photoreduction and evolution of mercury from seawater. The Science of the Total Environment, 261(2000): 125-135.

Covelli, S. et al., 2008. Benthic fluxes of mercury species in a lagoon environment (Grado Lagoon, Northern Adriatic Sea, Italy). Applied Geochemistry, 23(3): 529-546.

Covelli, S., Faganeli, J., Horvat, M. and Brambati, A., 1999. Porewater Distribution and Benthic Flux Measaurements of Mercury and Methylmercury in the Gulf of Trieste (Northern Adriatic Sea). 48(1999): 415-428.

Ensign, S.H., Halls, J.N. and Mallin, M.A.M.A., 2004. Application of digital bathymetry data in an analysis of flushing times of two large estuaries. Computers & Geosciences, 30(5): 501-511.

EPA, 1995. Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. EPA 821-R-95-027, Washington, DC.

EPA, 2001a. Appendix to Method 1631 Total Mercury in Tissue, Sludge, Sediment and Soil by Acid Digestion and BrCl Oxidation, pp. 13.

EPA, 2001b. Method 1630: Methylmercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS. EPA 821-R-01-020, Washington, D.C.

EPA, 2007. National Listing of Fish Advisories Technical Fact Sheet: 2005/06 National Listing, EPA-823-F-07-003.

Fitzgerald, W. and Mason, R.P., 1997. Biogeochemical cycling of mercury in the marine environment. Mercury and Its Effects on Environment and BiologyMetal Ions in Biological Systems. Marcel Dekker New York, 53–111 pp.

Fitzgerald, W.F., Lamborg, C.H. and Hammerschmidt, C.R., 2007. Marine Biogeochemical Cycling of Mercury. Chem. Rev., 107(2): 641-662.

Gagnon, C., Pelletier, E., Mucci, A. and Fitzgerald, W.F., 1996. Diagenetic Behavior of Methylmercury in Organic-rich Costal Sediments. 41(3): 428-434.

Geise, G.L., Wilder, H.B. and Parker, J., G.G., 1979. Hyrdology of Major Estuaries and Sounds of North Carolina, USGS.

Gill, G.A. et al., 1999. Sediment-Water Fluxes of Mercury in Lavaca Bay, Texas. Environmental Science and Technology, 33: 663-669.

Gilmour, C.C., Henry, E.A. and Mitchell, R., 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environ. Sci. Technol., 26(11): 2281-2287.

Guentzel, J.L. and Tsukamoto, Y., 2001. Processes influencing mecury speciation and bioconcentration in the North Inlet-Winyah Bay estuary, South Carolina, USA. Marine Pollution Bulletin, 42: 615-619.

Hammerschmidt, C.R. and Fitzgerald, W.F., 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. Environmental Science & Technology, 38(5): 1487-1495.

Hammerschmidt, C.R. and Fitzgerald, W.F., 2006. Photodecomposition of methylmercury in an arctic Alaskan lake. Environmental Science & Technology, 40(4): 1212-1216.

Hammerschmidt, C.R. and Fitzgerald, W.F., 2008. Sediment-water exchange of methylmercury determined from shipboard benthic flux chambers. Marine Chemistry, 109(1-2): 86-97.

Hammerschmidt, C.R., Fitzgerald, W.F., Balcom, P.H. and Visscher, P.T., 2008. Organic matter and sulfide inhibit methylmercury production in sediments of New York/New Jersey Harbor. Marine Chemistry, 109(1-2): 165-182.

Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., Balcom, P.H. and Visscher, P.T., 2004. Biogeochemistry of methylmercury in sediments of Long Island Sound. Marine Chemistry, 90(1-4): 31-52.

Han, S., Gill, G.A., Lehman, R. and Choe, K., 2006. Complexation of mercury by dissolved organic matter in surface waters of Galveston Bay, Texas. Marine Chemistry, 98(2006): 156-166.

Heyes, A., Mason, R.P., Kim, E.H. and Sunderland, E., 2006. Mercury methylation in estuaries: Insights from using measuring rates using stable mercury isotopes. Marine Chemistry, 102(1-2): 134-147.

Heyes, A., Miller, C. and Mason, R.P., 2004. Mercury and methylmercury in Hudson River sediment: impact of tidal resuspension on partitioning and methylation. Marine Chemistry, 90(1-4): 75-89.

Holmes, J. and Lean, D., 2006. Factors that influence methylmercury flux rates from wetland sediments. Science of the Total Environment, 368(1): 306-319.

Honeyman, B.D. and Santschi, P.H., 1988. Metals in aquatic systems. Environ. Sci. Technol., 22(8): 862-871.

Kieber, R.J., Whitehead, R.F. and Skrabal, S.A., 2006. Photochemical Production of Dissolved Organic Carbon From Resuspended Sediments. Limnology and Oceanography, 51: 2187-2195.

Kim, E.-H., Mason, R.P., Porter, E.T. and Soulen, H.L., 2006. The impact of resuspension on sediment mercury dynamics, and methylmercury production and fate: A mesocosm study. Marine Chemistry, 102(3-4): 300-315.

Kim, E.H., Mason, R.P., Porter, E.T. and Soulen, H.L., 2004. The effect of resuspension on the fate of total mercury and methyl mercury in a shallow estuarine ecosystem: a mesocosm study. Marine Chemistry, 86(3-4): 121-137.

King, J.K., Saunders, F.M., Lee Jr., R.F. and Jahnke, R.A., 1999. Coupling Mercury Methylation Rates to Sulfate Reduction Rates in Marine Sediments. 18(7): 1362-1369.

Krabbenhoft, D., Hurley, J., Olson, M. and Cleckner, L., 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. Biogeochemistry, 40(2): 311-325.

LaLonde, J.D., Amyot, M., Kraepiel, A.M. and Morel, F.M.M., 2001. Photooxidation of Hg(0) in Artificial and Natural Waters. Environmental Science and Technology, 35: 1367-1372.

Lalonde, J.D. et al., 2004. Photoinduced oxidation of Hg-0 (aq) in the waters from the St. Lawrence estuary. Environmental Science & Technology, 38(2): 508-514.

Lanzillotta, E., Ceccarini, C. and Ferrara, R., 2002. Photo-induced formation of dissolved gaseous mercury in coastal and offshore seawater of the Mediterranean basin. The Science of the Total Environment, 300(1-3): 179-187.

Lawson, N.M., Mason, R.P. and Laporte, J.-M., 2001a. The fate and transport of mercury, methylmercury, and other trace metals in chesapeake bay tributaries. Water Research, 35(2): 501-515.

Lawson, N.M., Mason, R.P. and Laporte, J.M., 2001b. The fate and transport of mercury, methylmercury, and other trace metals in Chesapeake Bay tributaries. Water Research, 35(2): 501-515.

Leermakers, M., Meuleman, C. and Baeyens, W., 1995. Mercury speciation in the Scheldt Estuary. Water, Air, & Soil Pollution, 80(1): 641-652.

Lin, C.-J. and Pehkonen, S.O., 1999. Aqueous Phase Reactions of Mercury with Free Radicals and Chlorine: Implications for Atmospheric Mercury Chemistry. Chemosphere, 38(6): 1253-1263.

Mallin, M.A., McIver, M.R. and Merritt, J.F., 2007. Environmental assessment of the Lower Cape Fear River system, 2006 Center for Marine Science, University of North Carolina at Wilmington, Wilmington, NC.

Manley, S.D., 2008. Concentration, Speciation and Dissolved Organic Matter Complexation of Mercury in Wilmington, NC Rainwater. MA thesis Thesis, University of North Carolina Wilmington, Wilmington, 82 pp.

Mason, R.P. et al., 1993. Mercury biogeochemical cycling in a stratified estuary. Limnology and Oceanography, 38(6): 1227-1241.

Mason, R.P., Fitzgerald, W.F. and Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochimica et Cosmochimica Acta, 58(15): 3191-3198.

Mason, R.P. and Lawrence, A.L., 1999. Concentration, Distribution, and Bioactivity of Mercury and Methylmercury in Sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. 18(11): 2438-2447.

Mason, R.P. et al., 1999. Mercury in the Chesapeake Bay. Marine Chemistry, 65(1-2): 77-96.

Mason, R.P. and Sullivan, K.A., 1998. Mercury and methylmercury transport through an urban watershed. Water Research, 32(2): 321-330.

Miller, C.L., Mason, R.P., Gilmour, C.C. and Heyes, A., 2007. Influence of Dissolved Organic Matter on the Complexation of Mercury Under Sulfidic Conditions. Environmental Toxicology and Chemistry, 26(4): 624-633.

Nriagu, J.O., 1994. Mechanistic steps in the photoreduction of mercury in natural waters. The Science of the Total Environment, 154: 1-8.

Parler, N.E., 2005. Mercury Concentration and Speciation in Coastal Rainwater. MA Thesis Thesis, University of North Carolina Wilmington, Wilmington, 76 pp.

Quemerais, B., Cossa, D., Rondeau, B., Pham, T.T. and Fortin, B., 1998. Mercury distribution in relation to iron and manganese in the waters of the St. Lawrence river. Science of the Total Environment, 213(1-3): 193-201.

Rolfhus, K.R. and Fitzgerald, W.F., 2001. The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY. Geochimica et Cosmochimica Acta, 65(3): 407-418.

Roth, D.A. et al., 2001. Distribution of inorganic mercury in Sacramento river water and suspended colloidal sediment material. Archives of Environmental Contamination and Toxicology, 40: 161-172.

Rothenberg, S.E., Ambrose, R.F. and Jay, J.A., 2008. Mercury cycling in surface water, pore water and sediments of Mugu Lagoon, CA, USA. Environmental Pollution, 154(1): 32-45.

Sager, D.R., 2002. Long-term variation in mercury concentrations in estuarine organisms with changes in relases into Lavaca Bay, Texas. Marine Pollution Bulletin, 44: 807-815.

Schroeder, W.H. and Munthe, J., 1998. Atmospheric mecury-An overview. Atmospheric Environment, 32: 809-822.

Selin, N.E. and Jacob, D.J., 2008. Seasonal and spatial patterns of mercury wet deposition in the United States: Constraints on the contribution from North American anthropogenic sources. Atmospheric Environment, 42(21): 5193-5204.

Sellers, P., Kelly, C.A., Rudd, J. and MacHutchon, A.R., 1996. Photodegradation of methylmercury in lakes. 380.

Shank, G.C., Skrabal, S.A., Whitehead, R.F. and Kieber, R.J., 2004a. Fluxes of strong Cu-complexing ligands from sediments of an organic-rich estuary. Estuarine Coastal and Shelf Science, 60(2): 349-358.

Shank, G.C., Skrabal, S.A., Whitehead, R.F. and Kieber, R.J., 2004b. Strong copper complexation in an organic-rich estuary: the importance of allochthonous dissolved organic matter. Marine Chemistry, 88(1-2): 21-39.

Skrabal, S.A., Donat, J.R. and Burdige, D.J., 1997. Fluxes of copper-complexing ligands from estuarine sediments. Limnol. Oceanogr., 42(5): 992-996.

Skrabal, S.A., Lieseke, K.L. and Kleber, R.J., 2006. Dissolved zinc and zinc-complexing ligands in an organic-rich estuary: Benthic fluxes and comparison with copper speciation. Marine Chemistry, 100(1-2): 108-123.

Stordal, M.C., Gill, G.A., Wen, L.S. and Santschi, P.H., 1996. Mercury phase speciation in the surface waters of three Texas estuaries: Importance of colloidal forms. Limnology and Oceanography, 41(1): 52-61.

Sunderland, E.M., Gobas, F.A.P.C., Branfireun, B.A. and Heyes, A., 2006. Environmental controls on the speciation and distribution of mercury in coastal sediments. Marine Chemistry, 102(1-2): 111-123.

Sunderland, E.M. et al., 2004. Speciation and bioavailability of mercury in well-mixed estuarine sediments. Marine Chemistry, 90(1-4): 91-105.

Szakacss, O., Lasztity, A. and Horvath, Z., 1980. Breakdown of organic mercury compounds by hydrochloric acid-permanganate or bromine monochloride solution for the determination of mercury by cold vapour atomic absorption spectrometry. Analytica Chimica Acta, 121: 219-224.

USGS, 2008. National Water Information System, USGS Water Data for the Nation, pp. http://waterdata.usgs.gov/nwis.

Wanninkhof, R., 1992. Relationship between wind-speed and gas-exchange over the ocean. Journal of Geophysical Research-Oceans, 97(C5): 7373-7382.

Whalin, L., Kim, E.-H. and Mason, R., 2007. Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. Marine Chemistry, 107(3): 278-294.

Xiao, Z.F., Stromberg, D. and Lindqvist, O., 1995. Influence of humic substances on photolysis of divalent mercury in aqueous solution. Water, Air, and Soil Pollution, 80: 789-798.

Zhang, H. and Lindberg, S.E., 2001. Sunlight and iron(III) induced photochemical production of dissolved gaseous mecury in freshwater. Environmental Science and Technology, 35: 928-935.