

Mercury Levels, Speciation, and Fate in Gulf Islands National Seashore Aquatic Systems

By

Mr. Sejin Youn, M.S. Graduate Assistant
Dr. Jean-Claude J. Bonzongo, P.I.

Dept. of Environmental Engineering Sciences
P.O. Box 116450, University of Florida
Gainesville, FL 32611-6450

Cooperative Ecosystem Studies Unit (CESU)
South Florida-Caribbean CESU

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ABSTRACT

The Gulf Islands National Seashore in southeastern USA gets on average about five million visitors every year. Amongst the multiple recreational activities attracting these visitors are both recreational and subsistence fishing. Unfortunately, mercury (Hg) levels in different environmental compartments of this park have not been studied and the potential for exposure to Hg by consumption of fish caught in the park's waters remains unknown. Following the discovery of high Hg levels in fish caught from Mobile Bay in Alabama, and based on the location of the Gulf Islands National Seashore park, the National Park Service (NPS) decided to conduct a set of studies that would help park managers to take appropriate decisions with regard to health risks to people visiting the park. In this study, we hypothesized that "Hg reaching the park waters from both runoffs and atmospheric deposition could result in fish Hg levels above safe limits, and therefore, to human exposure if the aquatic systems in and around the park have high potentials for methyl-Hg (MeHg) production and accumulation". This study was therefore initiated to assess both the levels and the extent of Hg contamination in different environmental compartments of selected sites within the park and to determine the potential for sediments collected from these sites to produce and accumulate MeHg. These objectives were addressed by a combination of field observational studies and laboratory investigations of Hg methylation and MeHg demethylation. Besides a few exceptions (e.g., sites with THg levels >10 ng/L), obtained results show rather low total Hg (THg) and MeHg levels in both water and sediment collected from most of the park units, with most of the determined concentrations falling within the range of background values reported in the literature. In addition, the ability of sampled sediments to produce and accumulate MeHg appears to be low as they tend to favor the degradation of MeHg over its production. Unfortunately, fish samples were not available for this first portion of the study. Despite the above observed favorable trends, our recommendation is that the complexity of Hg bioaccumulation and biomagnification processes in aquatic food chains warrants an investigation of Hg levels in fish and shellfish as the only effective way to address the issue of fish contamination in aquatic systems of the Gulf Islands National Seashore

1. INTRODUCTION

Mercury (Hg) has been used widely in science, industry, and agriculture because of its unique physicochemical properties. The current biggest consumers of Hg in the U.S. are the chlorine and caustic soda industries (U.S. EPA 1997, Adriano 2001). But Hg is also used in several other industrial (e.g., electrical and navigational equipment) and medicinal (e.g., dental amalgams, vaccines) (AAP and USPHS, 1999) activities. With regard to environmental pollution, the above anthropogenic activities have been linked primarily to point source pollution which tends to have local, and to some extent regional, pollution impacts. Of more serious concern is the combustion of fossil fuels that releases Hg directly into the atmosphere and a significant fraction of such released Hg is usually in the elemental form (i.e., Hg^0) (Boening, 2000). It has been estimated that in that specific form, Hg can have an atmospheric residence time that ranges from 0.7 to 2 years (Nater and Grigal, 1992). This rather long atmospheric residence time allows Hg to: (i) be transported over long distances, (ii) undergo chemical transformations such as oxidation in locations far away from point sources, and (iii) ultimately settle down in remote and pristine terrestrial and aquatic landscapes via both dry and wet precipitation. In addition to atmospheric deposition, runoffs and rivers do act as carrier for Hg that contaminates remote terminal basins/sinks (Heyes et al. 2004)

Concerns about the toxicity of mercury in the environment have increased since the notorious incident in Minamata Bay, Japan (Klein and Goldberg, 1970). This is due primarily to the ability of inorganic Hg to become methylated in sedimentary environments and to produce highly toxic and liposoluble alkyl-Hg species such as methyl mercury (MeHg). In consequence, the toxicity and methylation of Hg have driven most research on its environmental fate and transport, as well as its effects on living organisms. Because of the current increase in public awareness on health issues associated with Hg, mercury production which reached values as high as 6.7×10^3 tons/year in the 1970's is now on a steady decrease (Adirano, 2001; D'Itri, 1972), and in the US, the development of technologies that reduce Hg emissions associated with the burning of fossil fuels is strongly encouraged and funded by federal programs sponsored by US-DOE and US-EPA.

In 2001, the Mobile Register (Mobile, AL) reported that several popular commercial and recreational fish species caught in the Gulf of Mexico, including the restaurant delicacies amberjack, cobia and redfish, could contain very high Hg levels (Fig. 1), that they should not be sold to the public based on fish consumption standards set by the US Food and Drug Administration (FDA).

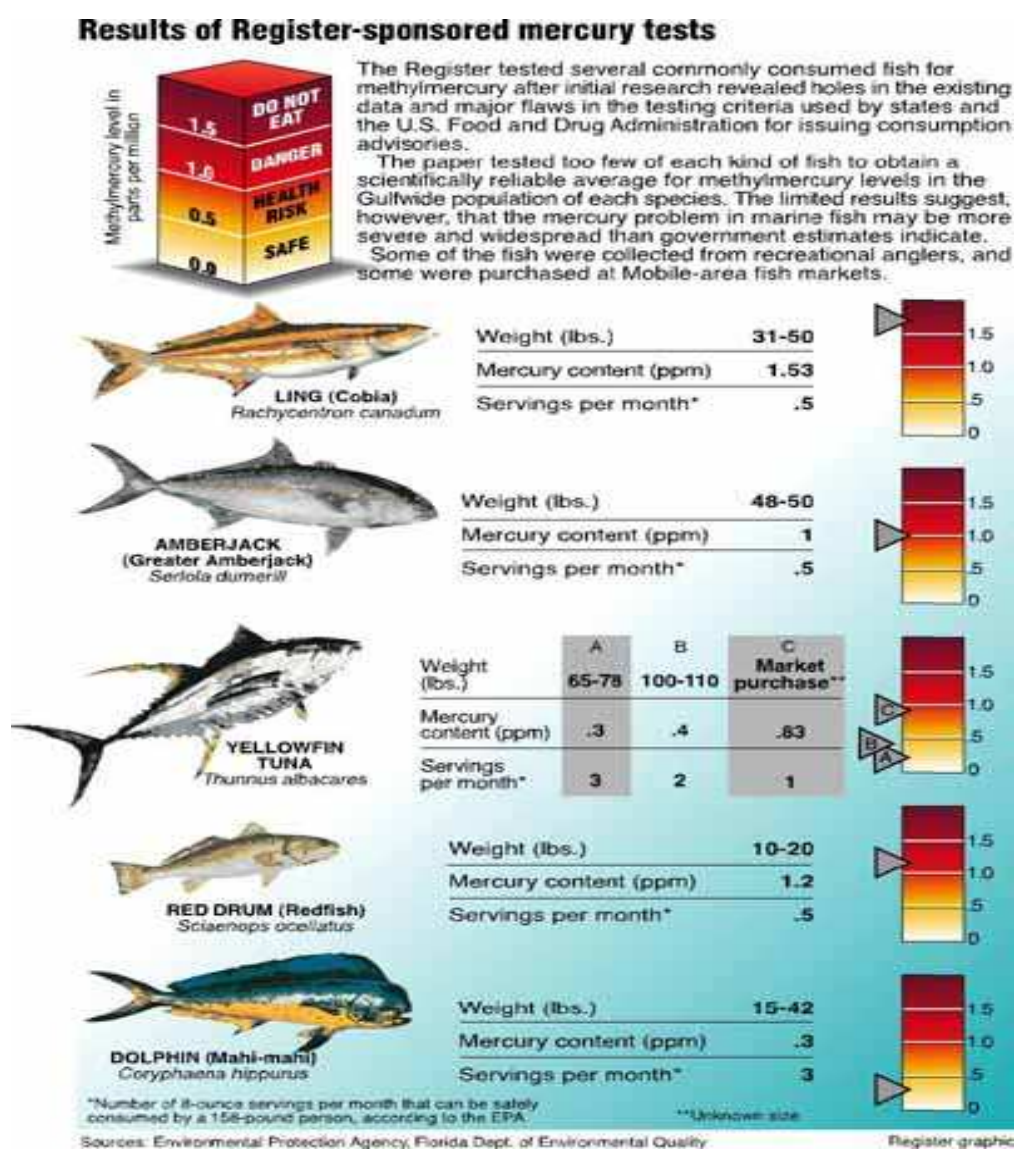


Figure 1: Result of mercury tests conducted by the Mobile Register and reported on 7/22/2001 in Mobile, AL.

Data posted on: <http://www.al.com/specialreport/mobileregister/?mercpc4.html>

In the past few decades, biogeochemical studies of Hg in aquatic systems have shown that remote and “*pristine*” systems removed from direct anthropogenic impacts could contain fish with Hg burdens exceeding safe guidelines for human consumption. In the southeastern USA, park’s water bodies located off the coast lines of Florida and Mississippi could receive Hg via both direct atmospheric deposition on terrestrial and aquatic landscapes and river transport of dissolved Hg to the Gulf of Mexico. Unfortunately, Hg levels in different environmental compartments in this national park remain unknown, despite the fact that they do host over five million visitors each year including people who come to camp and fish in park’s waters.

We hypothesized that “*Hg reaching the Gulf Island National Seashore from both river runoffs and direct atmospheric deposition could result in fish Hg levels above safe limits, and therefore, to human exposure if the aquatic systems in and around the park have high potentials for MeHg production and accumulation*”.

This study was initiated to: (1) assess both levels and the extent of Hg contamination, if any, in different environmental compartments of selected sites within the Gulf Islands National Seashore; and (2) to determine the potential of sediments in the park to produce and accumulate MeHg. These objectives were addressed by a combination of field observational studies and laboratory investigations of Hg methylation and MeHg demethylation.

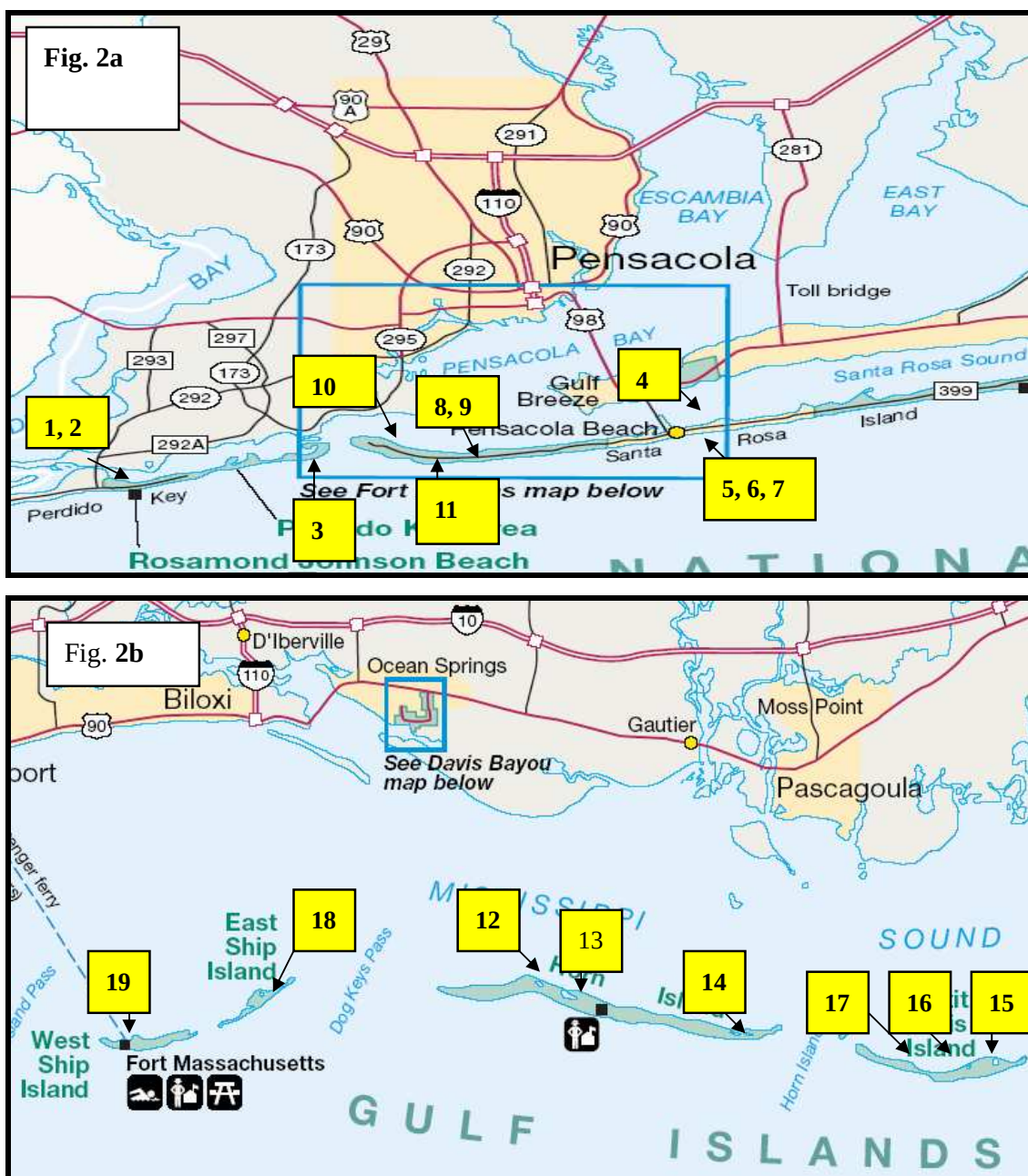
2 MATERIALS AND METHODS

2.1. Study site. This study focused on selected sites within the Gulf Islands National Seashore. The study area extended from Florida to Mississippi, and selected sampling sites included Fort Pickens (FP) on Santa Rosa Island, Naval Live Oaks (NLO), and Peridido Key (PK) in Florida (Fig. 2a). In Mississippi, samples were collected from Petit Bois, Horn, East Ship, and West Ship islands (Fig. 2b).

Based on the hypothesis stated earlier, the plan in this study was to collect water, sediment, and biota samples during both dry and rainy seasons. Due to budget limitations, the National Park Service (NPS) offered to provide us with all fish samples. Therefore, the sample collection effort by our

group focused on water, sediment and sea weed samples. Unfortunately, we never received fish samples during this study, and the succession of hurricanes in the study areas during this investigation did not allow us to follow our pre-planned sample collection campaigns.

Figure 2: Maps showing the geographical location of the park and sampling sites



Accordingly, data presented herein do not include fish Hg levels. With regard to water and sediment samples, presented data are obtained from samples collected during both the rainy and dry seasons for the islands located in Florida, and during the wet season only for sampling sites located in Mississippi. All collected sediments were used in laboratory experiments for the determination of potential rates of inorganic Hg methylation and methyl-Hg demethylation.

2.2. Sample collection and analytical techniques.

2.2.1. Water Samples: Surface water samples were collected in acid pre-cleaned Teflon[®] bottle with gloved hands, using the “ultra-clean free-metal sampling” protocol. In the laboratory, samples were acidified with optima[®]-HCl at a final concentration of 1% (v/v) and kept refrigerated at 4 °C until analysis. Only non-filtered samples were analyzed in this study. Therefore, reported Hg levels correspond to the sum of Hg bound to particulate matter and the truly dissolved Hg fraction. Total-Hg (THg) concentrations were determined in water samples after cold oxidation by bromine mono-chloride (BrCl) prior to reduction with SnCl₂ (Bloom and Crecelius, 1983). Methyl mercury (MeHg) was analyzed by direct ethylation of the water sample using sodium tetraethylborate (Bloom, 1989). In this latter case, MeHg compounds were stripped from solution, trapped on Tenax[®], transferred by heating onto a GC packed column (15% OV-3 on Chromosorb), and detected after separation and breakdown of alkyl-Hg compounds at ~800 °C by cold vapor atomic fluorescence spectrometry (CV-AFS). QA/QC procedures included instrument calibration using standard solutions, certified reference materials, duplicate analyses, and reagent blanks.

More details on these analytical procedures have been described in our group previous publications (e.g., Bonzongo and Lyons, 2004, Warner et al., 2003, 2005; Donkor et al., 2005; Donkor et al., 2006).

2.2.2. Collection and analysis of sediment and aquatic plant samples: Sediment samples were collected from all sampling sites by hand coring while sea weeds were simply grabbed from ocean floor by hands at near shore locations. In both cases, collected samples were placed into

clean polyethylene re-sealable bags and kept in the dark on ice in coolers until return to the laboratory on UF campus. THg in these solid samples was determined after hot acid digestion with concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture of a pre-weighed sample ($\sim 1\text{g}$) in acid-cleaned glass containers, heated overnight to a refluxing boil on a hot plate. After cooling and dilution with Nanopure[®] water, THg was determined by the SnCl_2 reduction technique and pre-concentration on gold followed by detection with CV-AFS.

MeHg in sediment and sea weed samples was determined following an alkaline alcohol ($\text{KOH}/\text{CH}_3\text{OH}$) digestion of $\sim 1\text{g}$ of sediment in an acid-cleaned screw capped Teflon vials and heating at 75°C . This step was then followed by aqueous ethylation of an aliquot of buffered digestate and MeHg determined as described earlier for water samples.

For both MeHg and THg, in addition to reagent blanks and standard solutions, a certified reference material (IAEA-405, estuarine sediments containing an average THg value of 0.81 mg Kg^{-1} and 5.49 ng g^{-1} for MeHg) was run with all digestions/analyses. The percent recovery on the IAEA-405 averaged $95 \pm 11\%$ ($n=10$), and $93 \pm 8\%$ ($n=10$) for THg and MeHg, respectively.

To determine the water and organic matter content in sediment samples, a specific amount of sediment was dried in oven for 12 hours at 105°C and water content calculated from the recorded loss of weight. This first step was then followed by combustion of the dried sample in a furnace for 2 hours at 550°C to determine the organic matter content as loss on ignition (LOI).

2.2.3 Laboratory determination of potential rates of Hg methylation (M) and MeHg degradation (D) in Gulf island National Seashore sediments: Potential Hg methylation and MeHg degradation assays were conducted according to the method of Pak and Bartha (1998) and as adapted by Warner et al. (2003). Measured sediments from each site were mixed with nanopure water (1:1; vol/vol). For each site, sediment were homogenized and apportioned into replicate centrifuge tubes (2-3 mL sediment in 45-mL tubes). Slurries were bubbled for 1 hour with ultra high purity (UHP) N_2 to accelerate the development of anaerobic conditions that favor Hg biotransformation. Individual tubes were then dosed with either HgCl_2 (for methylation experiments) or CH_3HgCl (for MeHg demethylation experiments) to a final concentration of 1ppm and 0.010ppm (or 10 ppb), respectively. Tubes were

incubated statically for 5 days at room temperature ($\sim 22^{\circ}\text{C}$) and in the dark. At the end of the incubation period, Hg biotransformation in the tubes was stopped by freezing and storage at -18°C until analysis. The M/D ratios of determined potential transformation rates (M = methylation and D = demethylation) were then used as parameter to assess the potential of each site to produce and accumulate MeHg.

3. RESULTS AND DISCUSSION

All data are presented in tables within the text and shown in figures appended at the end of this report

3.1. Mercury levels and speciation in the aqueous phase. During the dry season, water sample collection was limited to sites located in Florida and corresponding data are shown in Table 1a. In August 2004 (rainy season) our sampling campaign extended from Florida to Mississippi and data obtained from samples collected during this second field trip appear in Table 2. For sample sites located in Florida, Fig. 3 gives a comparative view of levels and trends of THg during both the dry and rainy seasons. The obtained results show that THg concentrations in these aquatic systems range from 0.19 ng L^{-1} to 14.26 ng L^{-1} (Table 1a) in the dry season and from 0.71 ng L^{-1} to 4.67 ng L^{-1} in the rainy season. About 69% of the analyzed samples fell within the range of calculated worldwide background THg values (0.1 to 3.5 ng L^{-1}) (Nriagu, 1990; Mason et al., 1994). The few samples with measured concentration $>5\text{ ng/L}$ in this study could be an indication of potential contamination from diffuse sources. In fact, in aquatic systems with well known sources of anthropogenic Hg inputs such as mining activities (e.g., the Carson River in Nevada, Idrija River in Slovenia, Madeira River in Brazil, and the Pra River in Ghana), mercury levels in the contaminated river sections vary from concentrations as low as 5 ng/L , which is similar to the highest values measured in this study, to thousands of ng/L near discharge points (e.g., Bonzongo et al. 2002; Donkor et al., 2006). However, these data will be better compared with data obtained from other coastal aquatic systems. Table 1b summarizes Hg levels reported in the literature for coastal waters worldwide. From this table, it is apparent that Hg levels measured in this study fall in the low end of reported Hg concentration ranges. It is worth noting that

besides its availability, the bioaccumulation of Hg in aquatic biota is site specific and Hg levels alone can not help predict levels in living tissues.

Table 1a: THg and MeHg in water sample collected from Peridido Key (PK), Fort Pickens (FP), Naval Live Oak island (NLO) in March, 2004 (**Value at detection limit); [§]P = pond; S = sea water)

Sample ID	Site description	Site #	THg (ng L ⁻¹)	MeHg (ng Hg L ⁻¹)
PK-1	Marsh	1	3.56	0.5**
PK-2	Marsh	2	2.92	0.5**
PK-3	Marsh	3	2.63	0.5**
NLO shallow	Inland pond with no contact with sea	4	1.18	0.7
NLO Beaver P [§]	Inland pond with no contact with sea	5	0.2	0.5**
NLO-2 P [§]	Inland pond with no contact with sea	6	10.46	0.5**
NLO-3 S [§]	Island seashore site	7	5.64	0.5**
FP P1	Inland pond	8	14.26	0.5**
FP P2	Island pond	9	0.19	0.5**
FP seashore-south	Island seashore site	10	6.57	0.5**
FP seashore-north	Island seashore site	11	4.29	0.5**
<i>n</i>			<i>11</i>	<i>11</i>
<i>range</i>			<i>0.19 - 14.26</i>	<i>0.5 - 0.7</i>
<i>mean</i>			<i>4.72</i>	<i>0.52</i>
<i>median</i>			<i>3.56</i>	<i>0.50</i>

Table 1b: Ranges of total and methyl mercury concentrations determined on water (ng/L) and sediment (ng/g) samples collected from coastal environments around the world.

Study location	Water (ng/L)		Sediment (ng/g)	
	THg	MeHg	THg	MeHg
Rio de Janeiro (Brazil)	3.64 - 11.04	—	120 - 440	—
Ria de Aveiro (Portugal)	1.0 - 275.4	—	100 - 51700	—
Eastern Lebanese sea (Lebanon)	0.31 - 0.44	—	—	—
The North Sea	0.18 - 0.96	—	—	—
South Florida Estuaries (USA)	3.0 - 7.4	<BDL to 2.3	1 - 219	<BDL to 0.49
Ulhas estuary (India)	40 - 610	—	80 - 190	—
North shore of Long Island (USA)	—	—	71.1 - 5250	—
Baltic sea (Poland)	—	—	37 - 880	0.01 - 2
South China Sea (Malaysia)	—	—	20 - 127	0.01 - 0.053
Bering sea (Russia)	—	—	77 - 112	0.1 - 0.62
Portuguese coast (Spain)	—	—	<BDL to 870	—
Bay of Fundy (Canada)	—	—	7 - 79	—
Kastela Bay (Croatia)	69 - 145*	—	14280 - 74000	6.05 - 36.74
Scheldt estuary (Belgium)	1.5	0.12	900	3.4
Gulf of Trieste (Italy)	50	0.2	38.4	2.9
Gulf of Mexico (USA – <i>This study</i>)	0.19 - 14.26*	0.5 - 1.58*	6.4 - 838	1 - 17

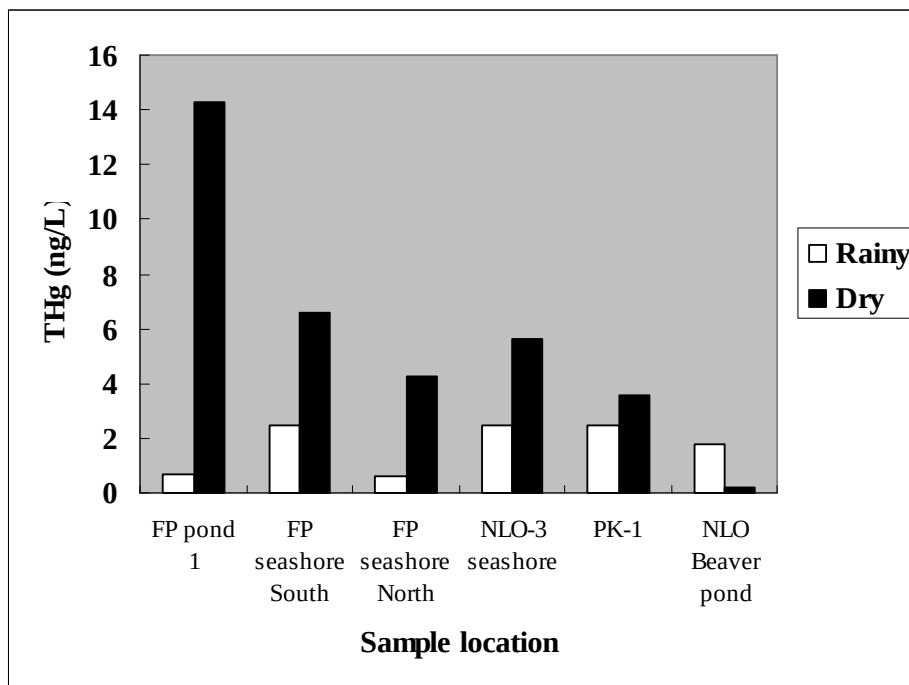
* *unfiltered; BDL: below the detection limit*

Table 2: THg and MeHg levels in water samples collected from sampling sites in both Florida and Mississippi in August, 2004.

Sample ID	site #	Site description	Wet season (August 2004)	
			THg(ng L^{-1})	MeHg (ng Hg L^{-1})
PK-1	1	Marsh	2.49	0.50
NLO Beaver	6	Inland pond	1.76	0.50
NLO-3	7	Island seashore site	2.48	0.56
FP P 1	8	Inland pond	0.71	0.50
FP P 2	9	Inland pond	n.d.*	n.d.*
FP seashore South	10	Island seashore site	2.46	0.50
FP seashore North	11	Island seashore site	0.62	0.61
PB West Pond	16	Inland pond with sea contact	0.57	0.50
PB West Pond	16	Island seashore site	1.77	0.50
PB interior	17	Inland pond with sea contact	0.75	0.50
PB interior	17	Island seashore site	0.88	0.50
PB lagoon	15	Inland pond with sea contact	3.58	1.04
PB lagoon	15	Island seashore site	2.64	0.66
Horn garden	14	Inland pond with sea contact	2.98	0.50
Horn garden	14	Island seashore site	2.38	0.61
Horn Ranger	13	Inland pond with sea contact	4.21	0.50
Horn Ranger	13	Island seashore site	n.d.*	n.d.*
Horn big lagoon	12	Inland pond with sea contact	3.24	1.02
Horn big lagoon	12	Island seashore site	3.55	0.50
East Ship	18	Inland pond with sea contact	4.67	1.58
East Ship	18	Island seashore site	3.11	0.89
West Ship	19	Inland pond with sea contact	0.75	0.50
West Ship	19	Island seashore site	2.08	0.50
<i>n</i>			21	21
<i>range</i>			0.57-4.67	0.5-1.58
<i>mean</i>			2.27	0.64
<i>median</i>			2.46	0.5

*n.d. = not determined

Figure 3: THg comparison of rainy season and dry season- aqueous phase



Comparatively, THg concentrations in samples collected during the dry season were higher than those measured in the wet season. Unlike most riverine systems where the rainy season brings a load of Hg-contaminated particles from watersheds resulting in high Hg levels in the aqueous phase (Hoff, 1996; Donkor et al., 2005), here rain seems to bring about dilution and higher THg levels are observed during the dry season. One possible explanation could be the very small ratio of the catchment area to open water surface. The Gulf Islands are “*barrier islands*” which extend over several miles from east to west off the coast of Florida and Mississippi. However, the catchment area of the different lacustrine systems (or ponds) found on each of the islands under study is usually very small, resulting in negligible inputs of terrestrial particulate matter and associated Hg into the aqueous phase. Overall, it appears that the addition of large volumes of rain/runoff water would tend to dilute the concentrations of Hg already present in these lacustrine systems. Lewis et al. (2002) reported THg concentrations up to 70 ng L^{-1} in waters samples collected from a control and a golf course impacted sites near Santa Rosa Sound. Although their high values seem to point to a clear sign of contamination, the paper does not elaborate on the sampling, storage, and the handling of analyzed samples. This aspect alone casts doubt on the validity of the data set published by Lewis et al. in 2002.

In contrast to THg concentrations which varied among sites, MeHg levels differed very little with a good number of measured values at or near our analytical detection limit of 0.5 ng L^{-1} to a maximum of

1.58 ng L⁻¹. These concentrations are similar to levels reported in the literature for other Southeastern USA aquatic systems with no known direct Hg inputs (Mastrine et al. 1999; Warner et al. 2005). No correlation ($r^2 = 0.0064$) was found between THg and MeHg, suggesting that the amount of MeHg in water did not depend on total amount of Hg present in the system. Also, since a significant fraction of MeHg observed in water comes from bottom sediment which is the primary site for MeHg production in aquatic systems, the observed low MeHg levels are therefore an indication of probable low Hg methylation potentials or low M/D ratios in the park water bodies. Data obtained from laboratory experiments and presented later herein tend to support this explanation.

3.2. Mercury levels and speciation in sediments. Concentrations of total and methyl Hg determined on non-sieved sediment samples ranged from 29 ng.g⁻¹ to 838 ng.g⁻¹ (average: 102.3 ng.g⁻¹) and from less than our analytical detection limit to 17 ng.g⁻¹ (average: 2.28 ng.g⁻¹), respectively. Corresponding data are presented in tables 3 and 4. For sampling sites located in Florida and where samples were collected during both the dry and rainy seasons, a trend similar to that of THg concentrations in water was observed (Fig. 4). The distribution of THg data followed the structural pattern of sediments, in that the accumulation of fine particles in top layers of sediments during the dry season overlapped with the highest THg concentrations, while the washout of these same fine particles during the rainy season left behind coarser sandy sediment with lower Hg content. This interpretation is based on simple visual observations since sediment size fractionation was not analyzed. Finally, the organic matter (OM) content in sediments was found to be a significant and positive function of sediment THg ($r^2=0.84$, $p<0.05$; Fig. 5), supporting the widely reported strong binding of Hg to organic matter in both freshwater and marine environments.

The highest concentrations of MeHg were measured in samples collected from Fort Pickens pond #1 (12 ng.g⁻¹) and Petit Bois (17 ng.g⁻¹). Both sites had very shallow water with surface sediments under less than 1 foot of water. Therefore high summer temperatures in addition to sulfate reducing bacteria (SRB) have probably played an important role in the production and accumulation of MeHg in these sites (e.g. Compeau and Bartha, 1985, Gilmour et al., 1992; Korthals and Winfrey, 1987, Bloom, 1999). When compared to MeHg data sets that are available in the peer reviewed literature, some of the numbers obtained in this study do largely exceed MeHg values reported from most aquatic systems with no known point sources of Hg (0.01-7.8 ng.g⁻¹) (e.g. Warner et al., 2005; Kannan, 1997; Bartlett and Craig, 1981). These MeHg data will be discussed further in relation with the ability of these sediments to produce and accumulate MeHg based on our laboratory experiments.

Figure 4: THg comparison of rainy season and dry season-sediment phase

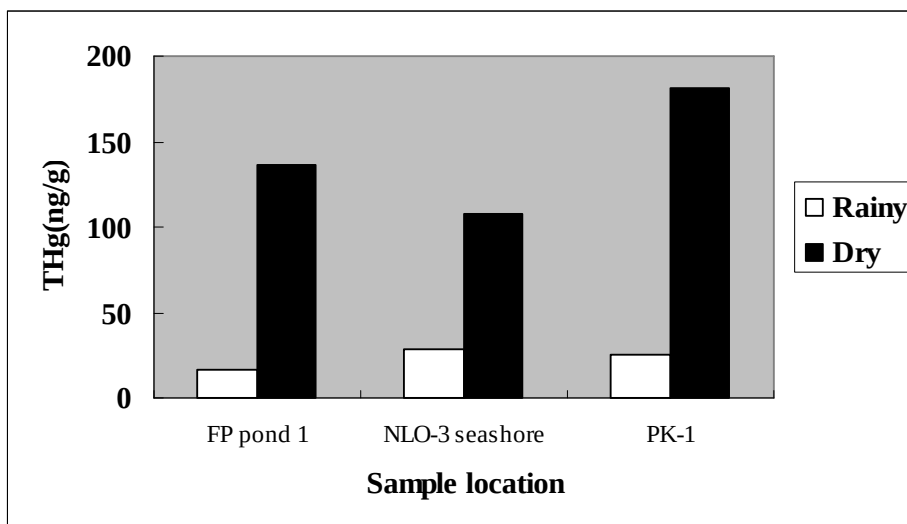


Figure 5: Relation ship between the concentration of THg and OM

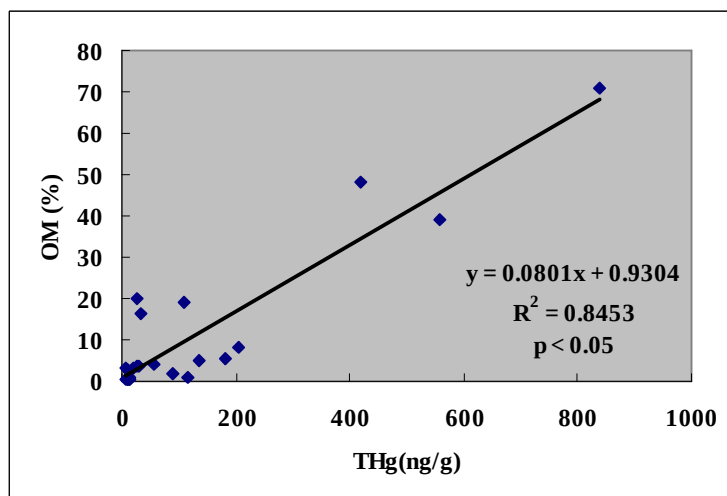


Table 3: THg and MeHg levels in sediment sample collected from PK, FP, NLO in March, 2004.
See Tables 1 and 2 for site description

Sample ID	Dry Season (March 2004)			
	THg(ng/g)	MeHg(ng/g)	Water content (%)	OM (%) as LOI
PK1	181	0.0005	50.19	5.43
PK1'	213	0.0005	48.27	4.51
PK2	558	0.0005	74.62	38.99
PK3	115	0.0005	25.98	0.9
PK3 Marsh	29	0.0005	51.86	4.54
NLO Shallow	418	0.0005	81.43	48.39
NLO Beaver	203	0.0005	44.88	7.78
NLO2 P	838	0.0044	85.54	71.17
NLO3 Seashore	108	0.0005	35.73	18.79
FP 1	136	0.0005	39.81	4.93
FP 2	56	0.0005	49.78	4.05
<i>n</i>	<i>11</i>	<i>11</i>	<i>11</i>	<i>11</i>
<i>range</i>	<i>29-838</i>	<i>0.0044-0.0005</i>	<i>25.98-81.43</i>	<i>0.9-71.17</i>
<i>mean</i>	<i>259.55</i>	<i>0.001</i>	<i>53.46</i>	<i>19.04</i>
<i>median</i>	<i>181</i>	<i>0.0005</i>	<i>49.78</i>	<i>5.43</i>

Table 4: THg and MeHg levels in sediment sample from PK, NLO, FP and PB in August, 2004. Inland pond

Sample ID	THg (ng.g ⁻¹)	MeHg (ng.g ⁻¹)	% Water content	% OM
PK-1	24.9	0.7	n.d	n.d
NLO-3 Seashore	28.4	5	n.d	n.d
FP P1	16.4	12	n.d	n.d
FP Seashore South	11.8	3.3	n.d	n.d
FP Seashore North	11.6	0.0005	n.d	n.d
PB West P	25.8	17	37.57	3.73
PB West S	9.3	4.2	20.98	0.41
PB interior P	6.4	4.9	48.19	3.36
PB interior S	11	0.0005	24.25	0.32
PB Lagoon P	10.3	3.1	32.31	2.6
PB Lagoon S	11.7	6.1	20.39	0.36
Horn Garden P	20.2	2.3	48.9	3.08
Horn Garden S	11.7	3	19.62	0.49
Horn Ranger P	26.7	1.2	19.59	20.05
Horn Ranger S	10.4	0.01	0.5	0.38
Horn big lagoon P	12.1	3.7	20.61	0.82
Horn big lagoon S	7.8	3	19.75	0.35
East Ship P	34.6	0.2	67.3	16.33
East Ship S	28.8	2.3	23.51	3.55
West Ship P	89.2	0.3	32.77	1.94
West Ship S	8.3	0.7	22.56	0.4
<i>n</i>	21	21	16	16
<i>range</i>	6.4-89.2	0.0005-17	0.5-67.3	0.32-20.05
<i>mean</i>	19.88	3.48	28.68	3.64
<i>median</i>	11.80	3.00	23.04	1.38

3.3. Mercury levels in plant tissues. Sea weeds were collected from 6 sites during the wet season only, and the determined THg concentrations in wet tissues ranged from 105 ng.g⁻¹ to 237 ng.g⁻¹ (Table 5). These measured THg concentrations were lower than values reported for most aquatic plants collected from salt marshes. For example, THg levels in wetland plants analyzed by Windham et al. (2003), ranged from 332.8 to 840 ng.g⁻¹. In contrast, in non polluted coastal water bodies, Lewis et al. (2004) measured THg concentrations (31 to 50 ng.g⁻¹) that were much lower than those determined in this study. The determination of the bioconcentration factor (BCF) defined as the ratio of THg concentrations in sea weeds to THg in water gave values in the order of 10⁴ to 10⁵ (Table 5). These calculated BCF values are much higher than those

reported by Lewis et al. 2004 (from 110 to 772), and suggest that despite the observed low THg and MeHg concentrations in water and sediment of the studied systems, bioaccumulation of Hg does occur. Therefore, organisms feeding on these sea weeds could accumulate Hg. Unfortunately we did not obtain biological tissues other than the analyzed plant materials. No relationship was found between Hg levels in sea weeds and sediments or water samples collected from corresponding sites. However, despite the lack of strong relationships between either water and plant THg or sediment and plant THg, the calculated BCF values suggested a clear tendency for Hg bioaccumulation. Since THg is not necessary equal to the bioavailable Hg fraction, the poor relationships described above could be due to Hg speciation and levels of bioavailable fractions in both water and sediments.

Owing to the restrictive root mechanism, Hg in plants tends to concentrate in roots (Gracey and Stewart, 1974a, Bony, 1971, De et al 1985, Greger, 2005). Windham et al. (2003) found that 70 to 100% of the metal concentration of whole plant was contained in the roots. Based on this observation, we speculate that higher THg levels are probably bio-accumulated in these sea weeds and this was likely not captured here as only leaves were analyzed in this study. This preliminary investigation needs to be followed by a well designed study to look at both Hg speciation in these plants and Hg levels in aquatic organisms that feed predominantly on them.

Table 5: THg concentrations in sea weeds in ng/g on wet weight basis and bio-concentration factors (BCF) determined as ratio of THg concentration in plant tissues over THg level in water

Sea weeds collected near the identified (#) sampling sites	THg in water expressed (ng.g ⁻¹)	THg in Sea grass (ng.g ⁻¹ , wet weight)	BCF (THg)
Horn Big Lagoon (#12)	0.00355	172.0	4.85 x 10 ⁴
Horn Garden (#14)	0.00238	111.9	4.70 x 10 ⁴
PB-Lagoon (#15)	0.00264	237.1	8.98 x 10 ⁴
PB-West Pond (#16)	0.00177	199.7	1.13 x 10 ⁵
PB-interior (#17)	0.00088	153.9	1.75 x 10 ⁵
East Ship (#18)	0.00311	105.9	3.41 x 10 ⁴
West Ship S(19)	0.00208	196.8	9.46 x 10 ⁴

3.4. Potential rates of Hg methylation and MeHg demethylation. Determined potential rates of Hg methylation (M), and MeHg demethylation (D) as well as calculated M/D ratios are given in Table 4. Potential rates of MeHg demethylation ranged from zero to 19.75% and potential rates of Hg methylation ranged from zero to 3.46%. M/D ratios have been widely used to compare the relative rates of Hg biotransformation from different environment types (e.g. Ramlal et al., 1986; Pak and Bartha, 1998; Warner et al., 2003). M/D ratios determined in this study ranged from zero when no Hg methylation was observed to 2.554. Note that only one site

(PK #1) in Florida had a M/D ratio >1. For every other tested sediments, the determined M/D ratios were <1 and orders of magnitude lower than the above mentioned maximum value. The assumption when using the M/D approach has been that the determined ratios would correlate with the observed ambient MeHg concentrations as they represent the net balance of the co-occurring processes of Hg methylation and MeHg demethylation. Unfortunately, our experimentally generated M/D ratios did not correlate well with ambient MeHg concentrations determined on sediment samples. Although factors controlling the net product of M and D remain poorly understood (Mason and Benoit, 2003), it is possible that in this study, M was maintained to very low values due to the addition of 1mg of Hg^{2+} per Kg of sediments with ambient THg concentration low ppb range (i.e., <0.09 mg/Kg). This significant increase in sediment THg concentration could have altered the sediment response by affecting the microbial population structure. In addition, the active sulfate reduction characteristics of the studied sediments (based on H_2S smell) could be an indication of abundant sulfide ligands that reduce Hg bioavailability to Hg-methylating agents via formation of insoluble HgS complexes (Ullrich et al., 2001). Also, the sediment organic matter content which tends to enhance methylation rates (Furutani and Rudd, 1980, Wright and Hamilton, 1982, Callister and Winfrey, 1986) was quite low in most of our sediment samples (Table 4). On the other hand, the use of only 0.01 mg of Hg added as CH_3HgCl per kg of sediments resulted in much higher potential rates of MeHg demethylation. This could also be due to the fact that D is rather less dependent upon aerobic and anaerobic conditions, and more dependent upon high pH (>7) common to these investigated systems (Matilainen, 1991). Overall, the M/D ratios determined in this study compare quite well with values reported for aquatic sediments by Gilmour and Henry (1991). Overall, for sediments with such low ambient THg levels, the use of trace stable isotopes to determine M and D would have been ideal (Hintleman et al., 1995, Rodriguez et al., 2004). Nevertheless, based on obtained data, it is likely that the production and accumulation of MeHg should be very limited in these systems and our experimental data support most of the observed low ambient MeHg levels determined by direct analysis of samples collected from the study sites. Recent reports show that the accumulation of Hg in biota, particularly in fish tissues of aquatic systems with no known Hg point source, is usually not correlated to MeHg levels in sediments (Warner et al. 2005). This lack of direct relationship finds its explanation in the complexity of the bioaccumulation process and to the poorly known number of steps and mechanisms that lead to the transfer of Hg from sediment following sedimentary biotransformation of inorganic Hg to MeHg to biota.

Table 6: Potential rates of Hg methylation (M) and MeHg demethylation (D) and M/D ratios.

Location	Demethylation (%)	Methylation (%)	M/D ratio
PK P1	0.13	0.33	2.554
PK P2	10.05	0.43	0.042
PK-2 S	19.10	0.14	0.007
PK-3 S	17.21	0.12	0.007
PK3 Marsh	18.38	0.69	0.038
NLO Shallow - P	1.12	0.13	0.120
NLO Beaver - P	17.49	0.26	0.015
NLO-2 P	0.00	0.12	-
NLO-3 S	19.03	0.00	0.000
FP P1	19.75	0.24	0.012
FP P2	0.00	0.21	-
PB West P	9.45	0.41	0.043
PB West S	10.94	0.11	0.010
PB Interior P	1.56	0.17	0.110
PB Interior S	4.51	0.00	0.000
PB Lagoon P	6.03	0.00	0.000
PB Lagoon S	4.63	0.00	0.000
Horn Garden P	9.86	0.11	0.011
Horn Garden S	19.21	0.09	0.005
Horn Ranger P	1.01	0.05	0.054
Horn Ranger S	6.39	0.00	0.000
Horn Big Lagoon P	3.26	0.06	0.018
Horn Big Lagoon S	2.25	0.02	0.011
East Ship P	16.53	0.31	0.019

S = seashore; P = inland ponds

4. CONCLUSIONS AND RECOMMENDATIONS

This preliminary examination of Hg levels and speciation in different environmental compartments of the studied park has shown that water, sediments, and aquatic plants in the park have relatively low THg and MeHg and can be considered non-polluted based on background values reported in the literature, as well as the safe guideline criteria for water and sediments. However, fish with Hg levels above the World Health Organization (WHO) safe limits have been recorded in many aquatic systems where Hg levels do fall within the so-called background levels. This is because the bioaccumulation of Hg depends not only on Hg levels, but also on site specific conditions. Based on data obtained in this study, the ability of sampled sediments to produce and accumulate MeHg appears to be low. Therefore, one could anticipate a relatively low Hg bioaccumulation in biota of these coastal environments. However, and as stated above, the complexity of Hg bioaccumulation and biomagnification in aquatic food chains may not support the above conclusion (Gorski et al., 2003). We therefore recommend an investigation of Hg levels in fish and shellfish as the only effective way to address the issue of fish contamination in these aquatic systems.

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REFERENCES

- AAP and USPHS (1999) Joint statement of the American academy of pediatrics and the United States Public health service, *Pediatrics* 104:568-568
- Adriano DC (2001) *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metal.*, Springer-Verlag, 2nd ed, New York, USA
- Balogh SJ, Huang Y, Offerman HJ, Meyer ML, Johnson DK (2003) Methylmercury in rivers draining cultivated watersheds, *Sci Total Environ* 304:305-313
- Bartlett PD, Craig PJ (1981) Total mercury and methyl mercury levels in British estuarine sediments-II *Water Res.* 15:37-47
- Bloom NS, Crecelius EA (1983) Determination of mercury in seawater at sub-nanogram per liter levels *Marine Chem* 14(1): 49-59
- Bloom NS (1989) Determination of picogram levels of methylmercury by aqueous phase ethylation followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Can J. Fish Aquat. Sci.* 46:1131-1140
- Boening DW (2000) Ecological effects, transport, and fate of mercury: a general review. *Chemosphere* 40:1335-1331
- Boney AD (1971). Sub-lethal effects of mercury on marine algae. *Mar. Pollut. Bull.*, 2:269-71
- Bonzongo JC, Lyons WB (2004) Impact of land use and physicochemical settings on aqueous methylmercury levels in the Mobile-Alabama River System. *Ambio* 33(6):329-33
- Bonzongo, J.C., W.B. Lyons, M.E. Hines, J.J. Warwick. (2002). Mercury in surface waters of three mine-dominated aquatic systems: Idrija River, Slovenia; Carson River, Nevada USA; and Madeira River, Brazil. *Geochemical Exploration and Environmental Analysis*, 2(2): 111-120
- Callister SM, Winfrey MR (1986) Microbial methylation of mercury in Upper Wisconsin river sediments. *Water Air Soil Pollut* 29:453-265
- Compeau G, Bartha R (1985) Sulfate-Reducing Bacteria: Principal Methylator of Mercury in Anoxic Estuarine Sediment. *Appl. Environ Microbiol* 50:499-502
- Compeau G, Bartha R (1984) Methylation and demethylation of mercury under controlled redox, pH, and salinity conditions. *Appl Environ Microbiol* 48:1203-1207
- De AK, Sen AK, Modak DP, Jana S (1985) Studies of toxic effects of Mercury II on *Pistia Stratiotes*. *Water Air and Soil Pollut* 24:351-360
- Donkor, A.K., Bonzongo, J.C., Nartey, V.K., and Adotey[†], D.K. (2006). Mercury in different

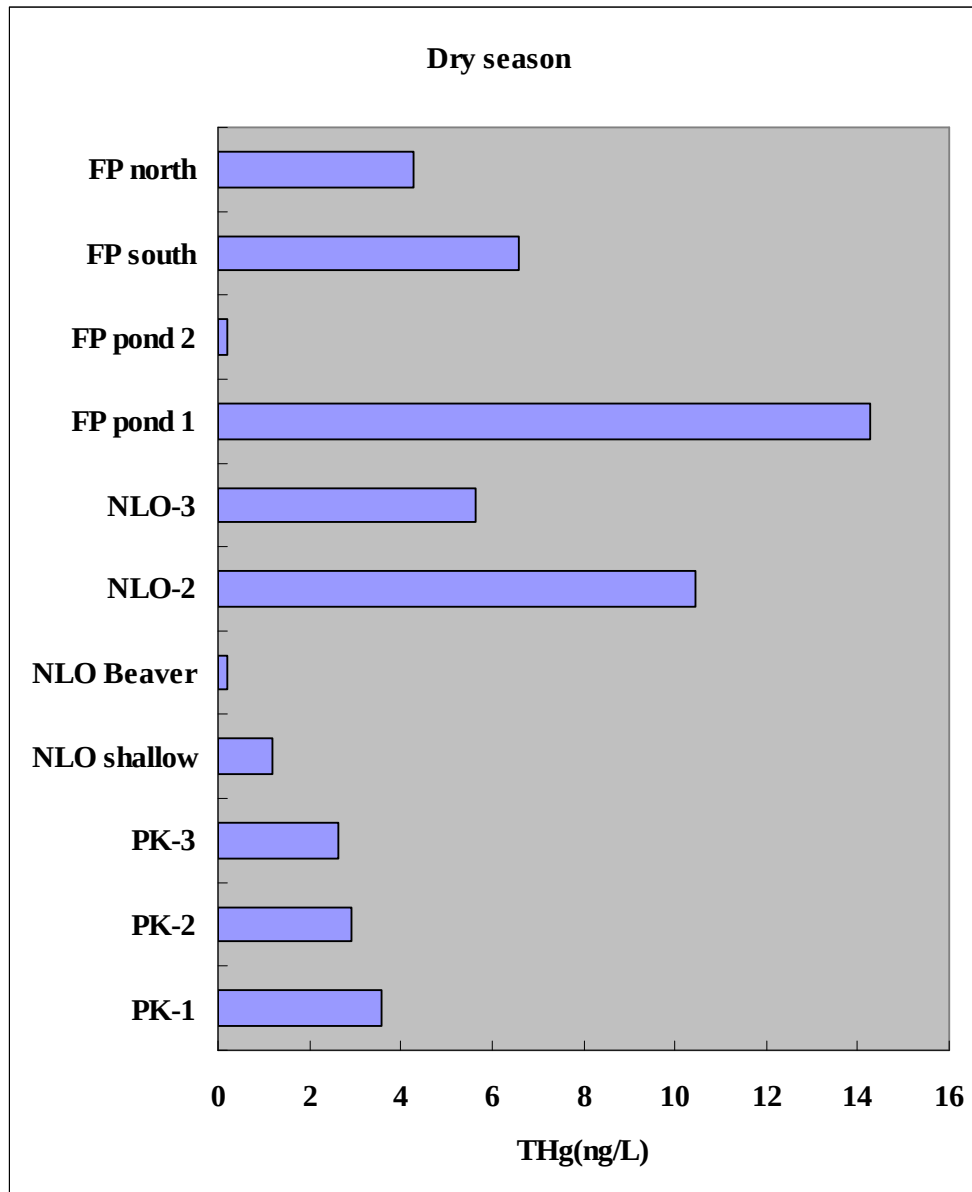
- environmental compartments of the Pra River basin, Ghana. *Science of the Total Environment*, 368: 164-176
- Donkor AK, Bonzongo JC, Nartey VK, Adotey DK (2003) Heavy metals in Sediments of the Gold mining Impacted Pra River Basin, Ghana, West Africa. *Soil Sediment Contam* 14:479-503
- Donkor AK, Bonzongo JC, Nartey VK, Adotey DK (*In press*) Mercury in different environmental compartments of the Pra River Basin, Ghana. *Science of Total Environ*
- D'Itri FM (1972) *The Environmental Mercury Problem*, CRC Press, Cleveland, USA
- Furutani A, Rudd JWM (1980) Measurement of mercury methylation in lakewater and sediment samples. *Appl Environ Microbiol* 40:770-776
- Gilmour CC, Henry EA (1991) Mercury methylation in aquatic systems affected by acid deposition. *Environ Pollut* 71:131-169
- Gilmour CC, Henry EA, Mitchell R (1992) Sulfate stimulation of Mercury Methylation in Freshwater sediments. *Environ Sci Technol* 26(11):2281-2287
- Gorski PR, Cleckner LB, Hurley JP, Sierszen ME, Armstrong DE (2003) Factors affecting enhanced mercury bioaccumulation in inland lakes of Isle Royale National Park, USA. *Sci Total Environ* 304(1-3):327-348
- Gracey HI, Stewart JWB (1974a) In proc Conf Land Waste management Ottawa, Ontario, Canada
- Gray JE, Fey DL, Holmes CW, Lasorsa BK (2005) Historical deposition and fluxes of mercury in Narraquinnep Reservoir, southwestern Colorado, USA. *Appl Geochem* 20:207-220
- Greger M, Wang Y, Neuschütz C (2005) Absence of Hg transpiration by shoot after Hg uptake by roots of six terrestrial plant species *Env Pollut* 134(2):201-208
- Heyes A, Miller C, Mason RP (2004) Mercury and methyl mercury in Hudson River sediment: Impact of tidal resuspension on partitioning and methylation. *Marine Chem* 90:75-89
- Hintelmann H, Douglas Evans R, Villeneuve JY (1995) Measurements of mercury methylation in sediments by using enriched stable mercury isotopes combined with methyl mercury determination by gas chromatography-ICP-MS. *J Anal At Spectrom* 10:619-624
- Hoff RM, Strachan WMJ, Sweet CW, Chan CH, Shackleton M, Bidleman TF, Brice KA, Burniston DA, Cussion S, Gatz DF (1996) Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. *Atmospheric Environment* 30(20):3505-3527
- Kannan K, Smith RG, Lee RF, Windom HL, Heitmuller PT, Macauley JM, Summers JK (1998) Distribution of Total Mercury and Methyl Mercury in Water, Sediment, and Fish from South Florida Estuaries. *Arch Environ Contam Toxicol* 34:109-118
- Korthals ET, Winfrey, MR (1987) Seasonal and Spatial Variations in Mercury Methylation and Demethylation in an Oligotrophic Lake. *Appl Environ Microbiol* 53(10):2397-2404
- Klein DH, Goldberg ED (1970) Mercury in the marine environment. *Environ Sci Technol* 4(9):765-768
- Lewis MA, Boustany RG, Dantin DD, Quarles RL, Moore JC, Stanely RS (2002) Effects of a Coastal Golf Complex on Water Quality, Periphyton, and Seagrass. *Ecotox Environ Safe* 53:154-162

- Lewis MA, Quarles RL, Dantin DD, Moore CJ (2004) Evaluation of a Florida coastal golf complex as a local and watershed source of bioavailable contaminants. *Marine Pollut Bull* 48(3-4):254-262
- Lindqvist O(1991) Mercury in the Swedish environment, recent research on causes, consequences and corrective methods. *Water Air Soil Pollut* 55:1-261
- Lyons WB, Welch KA, Bonzongo, JC (1999) Mercury in aquatic systems in Antarctica. *Geophys Res Lett* 26(15):2235-2238
- Mason RP, Benoit JM (2003) *Organometallic Compounds in the Environment*, Wiley, West Sussex, UK
- Mastrine JA, Bonzongo JC, Lyons WB (1999) Mercury concentration in surface waters from fluvial systems draining historical precious metals mining areas in southeastern USA. *Appl Geochem* 14:147-158
- Mason RP, Fitzgerald WF, Morel FMM (1994) The biogeochemical cycling of elemental mercury: anthropo- genic influences. *Geochim Cosmochim Acta* 58:3191-3198
- Matilainen T, Verta M, Niemi M, Uusiauva A (1991) Specific rates of net methylmercury production in lake sediments. *Water Air and Soil Pollut* 56:595-605
- Nater EA, Grigal DF (1992) Regional Trends in Mercury Distribution across the Great Lakes States, North Central USA. *Nature* 358:139-141
- Nriagu JO (1990) Human influence on the global cycling of trace metals. *Palaeogeog Palaeoclim Palaeoecol* 82:113-120
- Roriguez Martin-Doimeadios RC, Tessier E, Amouroux D, Guyoneaud R, Duran R, Caumette P, Donard OFX (2004) Mercury methylation/demethylation and volatilization pathways in estuarine sediment slurries using species-specific enriched stable isotopes *Marine Chemistry*. 90(1-4):107-123
- Swain EB, Engstrom DR, Bringham ME, Henning TA, Brezonik PL (1992) Increasing rates of atmospheric deposition in mid-continental North America. *Science* 257:784-787
- Ullrich SM, Tanton TW, Abdrashitova SA(2001) Mercury in the aquatic environment: a review of factors affecting methylation. *Crit Rev Env Sci Tec* 31(3):241-293
- US-EPA (1996) Mercury Study Report to Congress, Vol 1: Executive Summary US-EPA/R-97-003, NTIS, Springfield, VA.
- Warner KA, Roden EE, Bonzongo JC (2003) Microbial Transforamtion in Anoxic Freshwater Sediments under Iron-Reducing and Other Electron-Accepting Condition. *Environ Sci Technol* 37:2159-2165
- Waner KA, Bonzongo JC, Roden EE, Ward GM, Green AC, Chaubey Indrajeet, Lyons WB, Arrington DA (2005) Effect of watershed paramethers on mercury distribution in different environmental compartments in the Mobile Alabama River Basin, USA. *Sci Total Environ* 347:187-207
- Windham L, Weis JS, Weis P (2003) Uptake and distribution of metals in two dominant marsh macrophytes, *Spartina alterniflora* (cordgrass) and *Phragmites australis* (common reed) Estuarin, Coastal and Shelf. *Science* 56(1):63-73

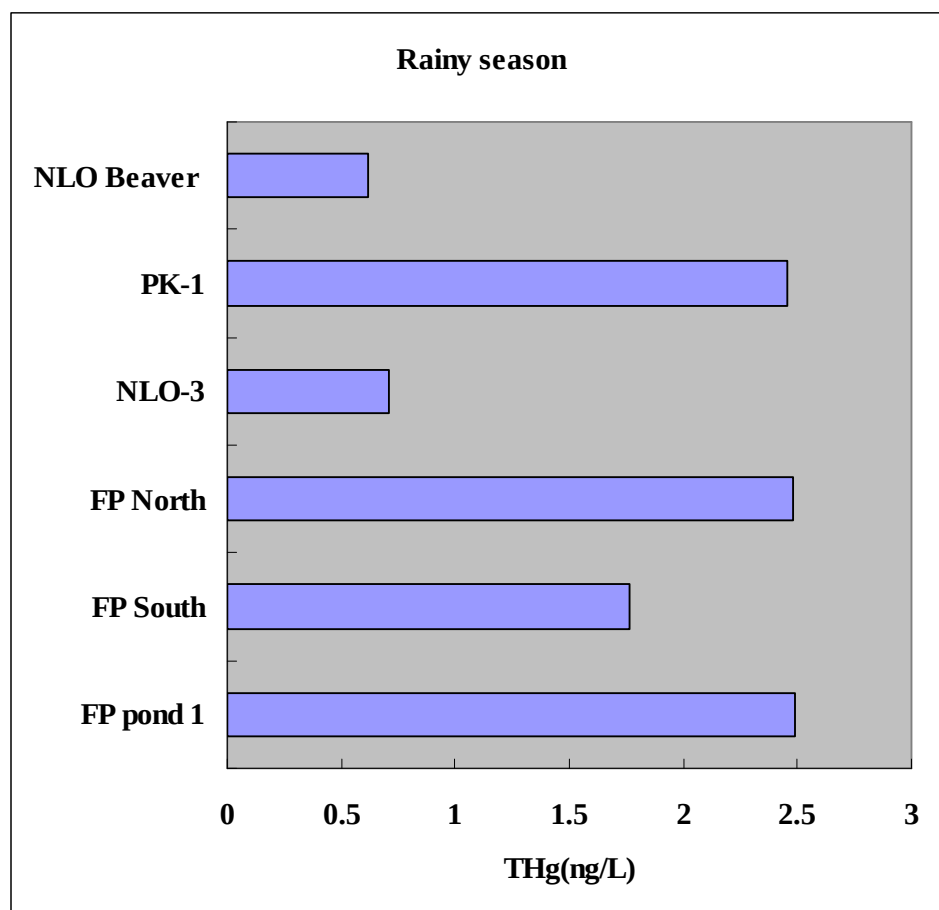
- Wright DR, Hamilton RD (1982) Release of methyl mercury from sediments: effects of mercury concentration, low temperature and estuarine environment, *Can J Fish Aquat Sci* 39:1459-1466
- Vandal GM, Mason RP, McKnight D, Fitzgerald W (1998) Mercury speciation and distribution in a polar desert lake (Lake Hoare, Antarctica) and two glacial meltwater streams. *Sci Total Environ* 213:229-237

APPENDICES

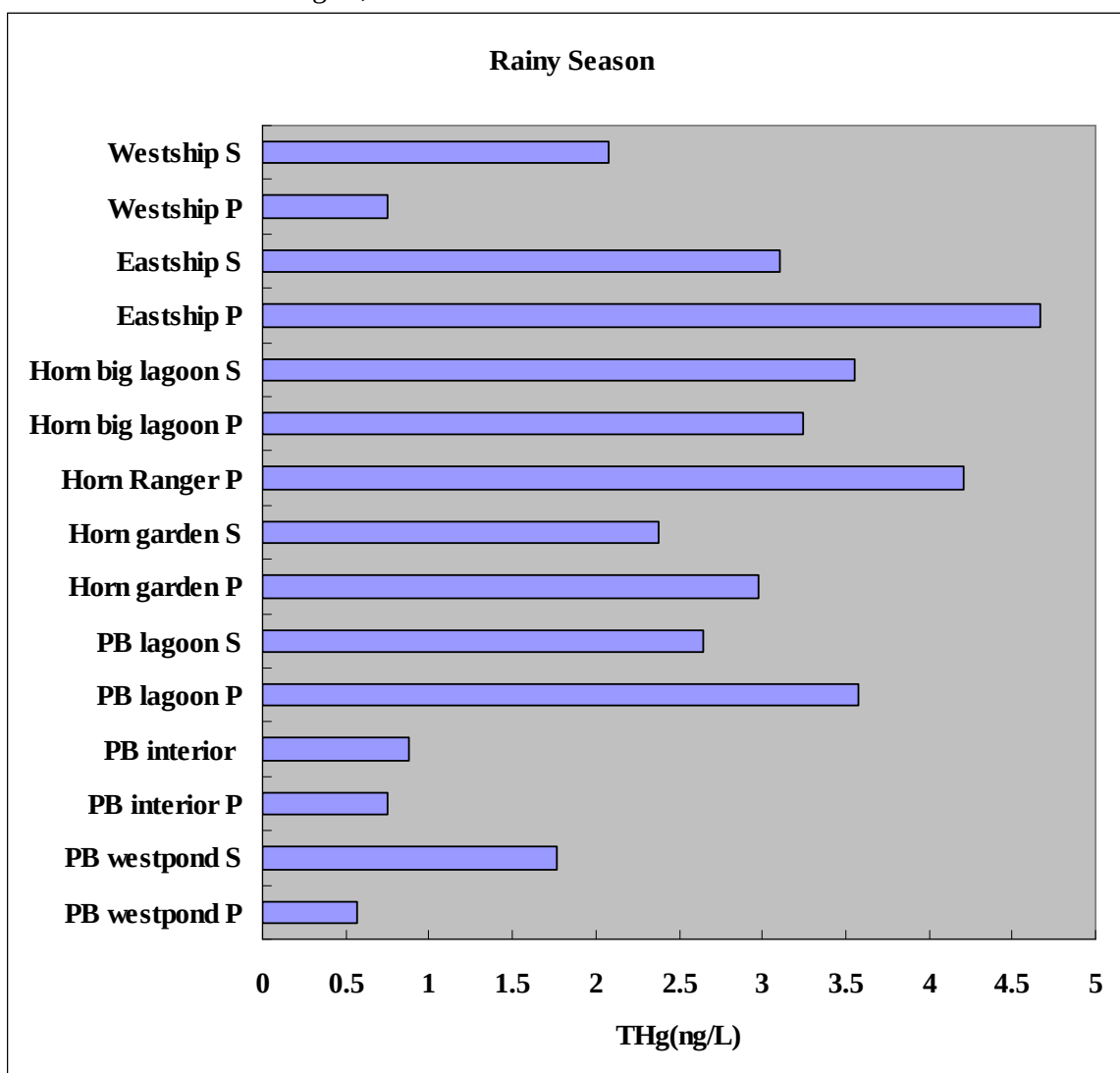
Appendix A: Graphic representation of THg data in water collected from sampling sites in Florida. March, 2004



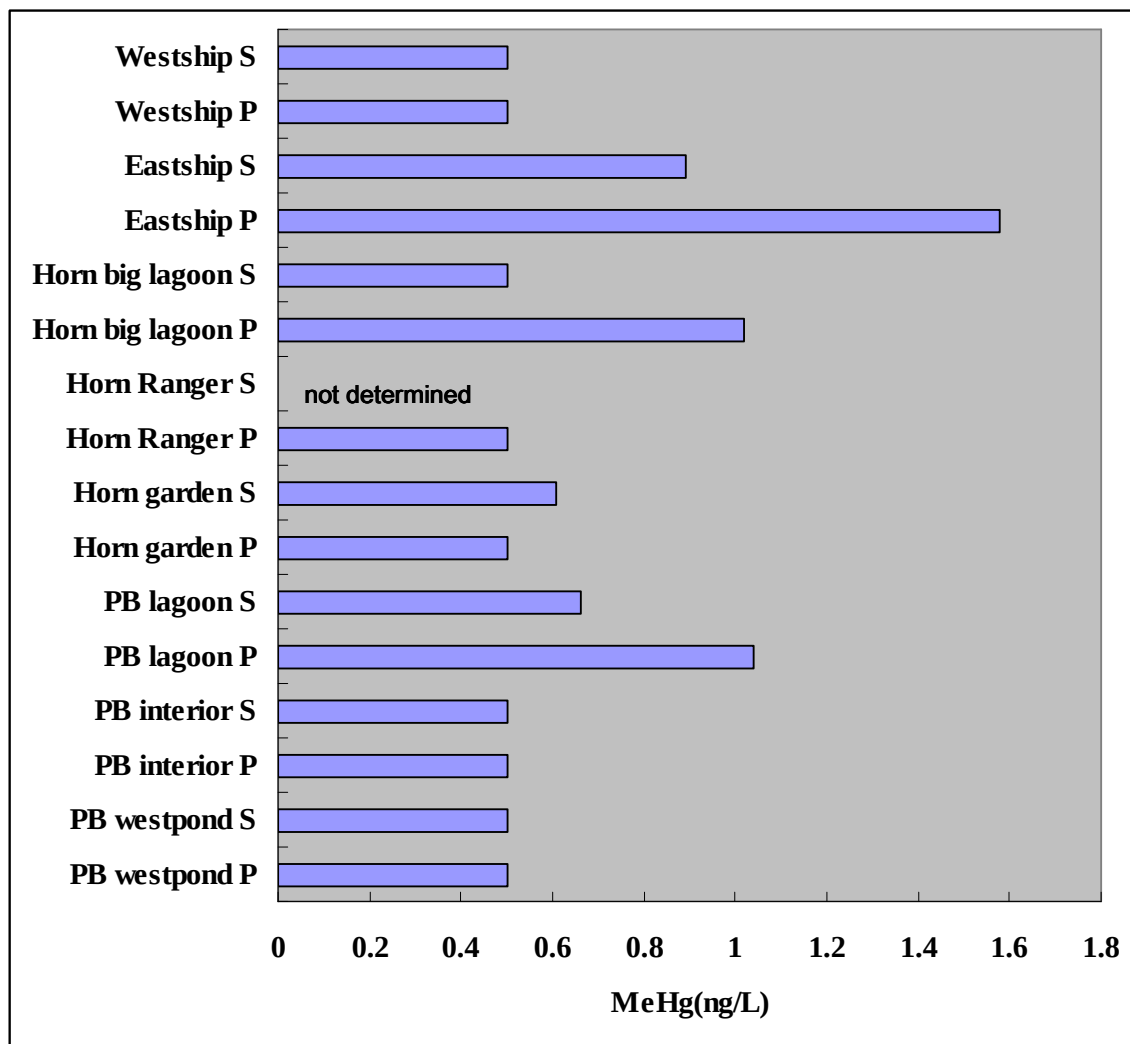
Appendix B: Graphic representation of THg data in water collected from sampling sites in Florida. August, 2004



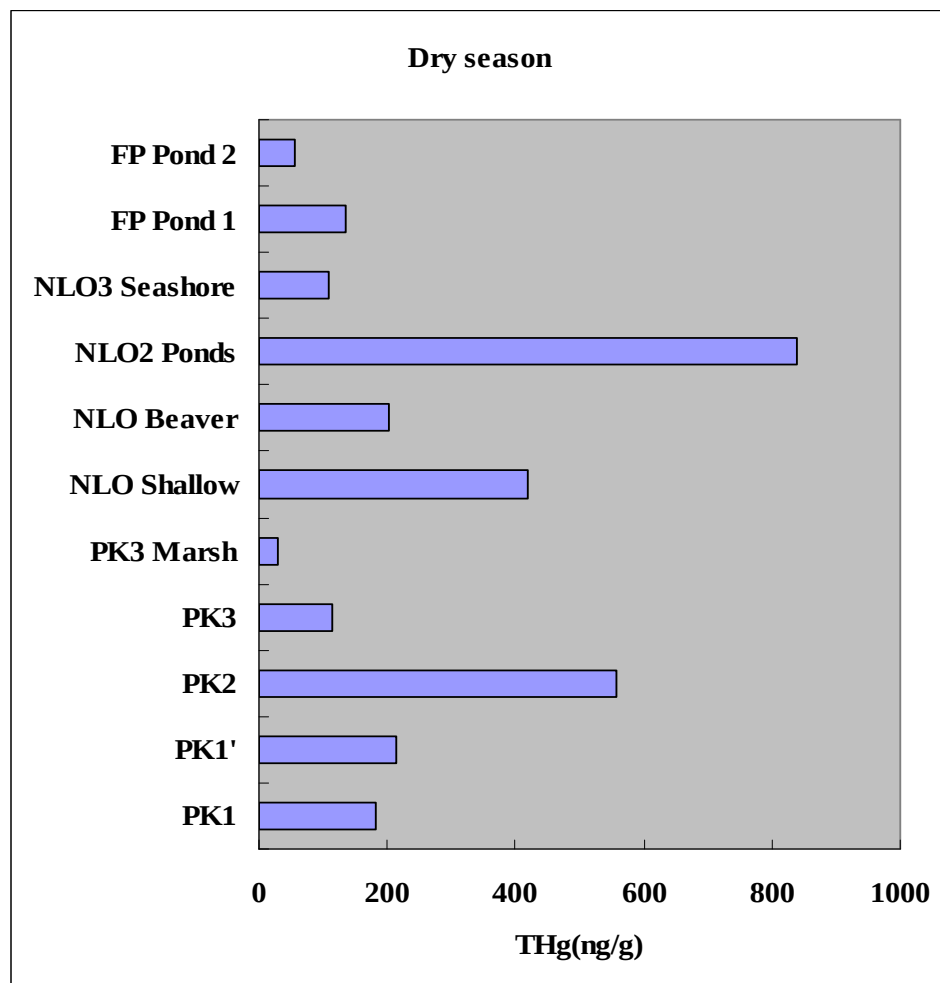
Appendix C: Graphic representation of THg data in water samples collected from sampling sites in Florida. August, 2004



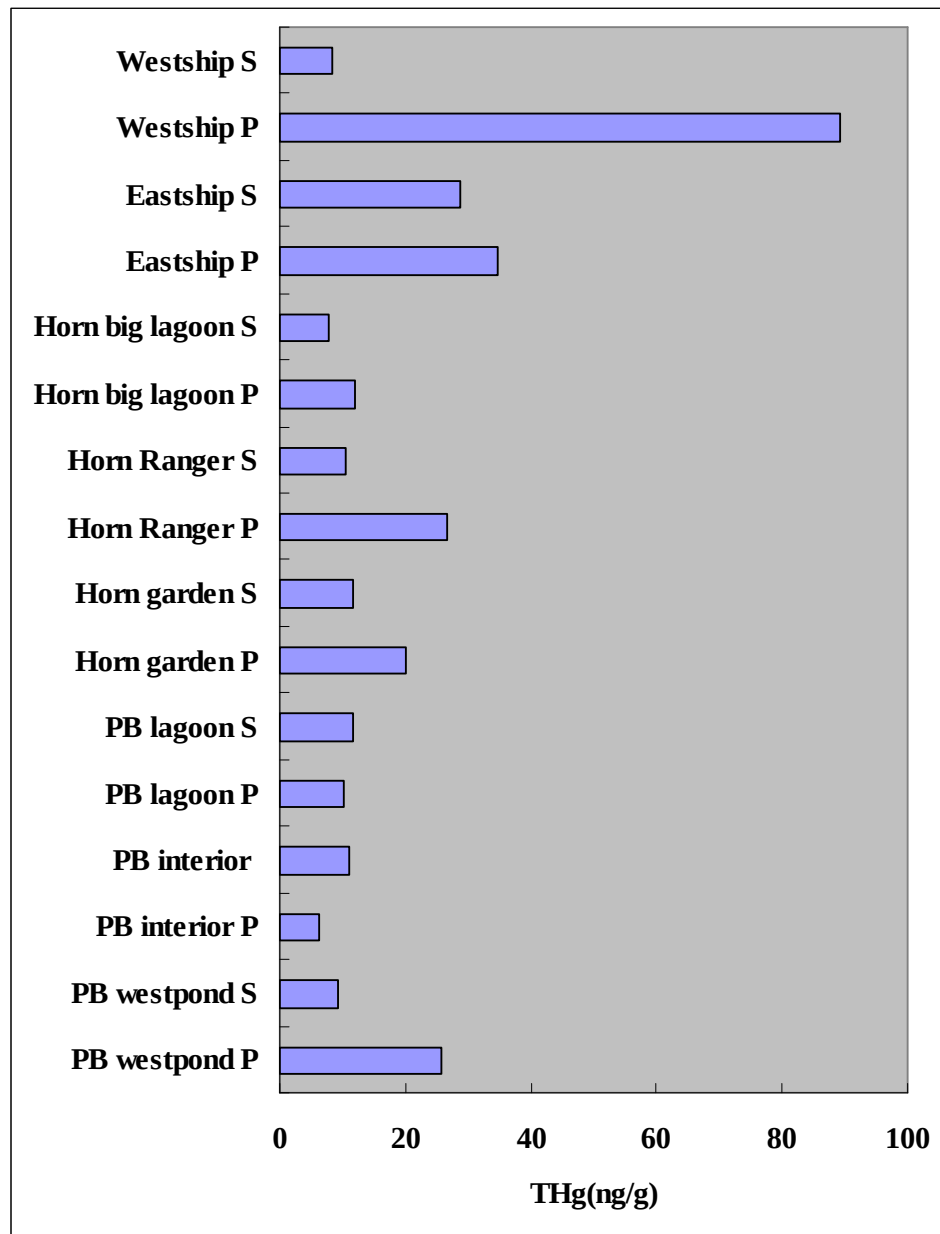
Appendix D: Graphic representation of MeHg data in water samples collected from sampling sites in Mississippi - August, 2004



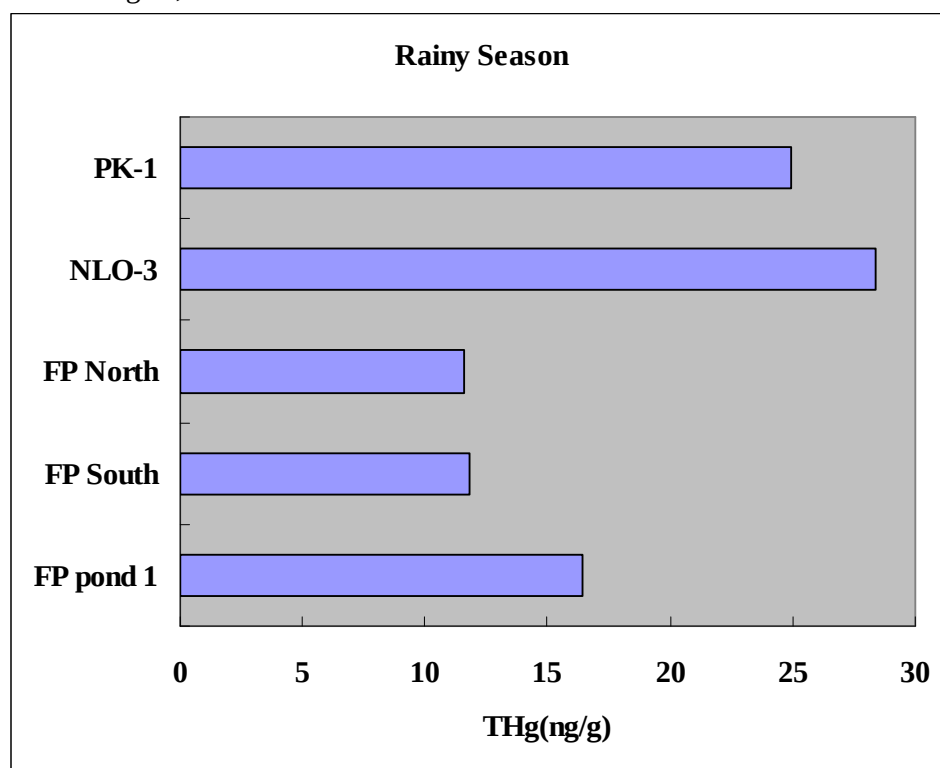
Appendix E: Graphic representation of THg data in Sediments collected from sampling sites in Florida. March, 2004



Appendix F: Graphic representation of THg data in Sediments collected from sampling sites in Mississippi, August, 2004



Appendix G: Graphic representation of THg data in Sediments collected from sampling sites in Florida. August, 2004



Appendix H: Graphic representation of MeHg data in sediments collected from sampling sites in Mississippi - August, 2004

