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Mercury in Aquatic Systems of the Gulf Islands National Seashore, Southeastern USA

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ABSTRACT: This study reports on levels and speciation of mercury (Hg) in different environmental compartments of selected park units in the Gulf Islands National Seashore (USA), and on potential rates of methyl-Hg (MMHg) formation and degradation in sediments. In the aqueous phase, total (THg) and MMHg concentrations ranged from 0.19 to 14.26 ng/L (*n=32*) and <0.5 to 1.58 ng/L (*n=32*), respectively. In sediments, THg concentrations varied from 6.4 to 838 ng/g wet weight (*n=32*), while MMHg levels ranged from 1 to 17 ng/g (*n=21*). Potential rates of MMHg formation (M) and degradation (D) in sediments resulted in M/D ratios that were mostly <1, suggesting a low tendency for accumulation of produced MMHg in these sediments. Finally, the detection of THg concentrations averaging 168.18 ± 48 ng/g in tissues of *Ulva prolifera* points to the tendency of Hg bioaccumulation, and therefore, the need for investigation of Hg levels in fish and shellfish. Overall, our findings show that coastal waters and sediments with very low Hg concentrations could support Hg-contaminated biota, which should justify the need for stringent regulations on Hg introduction to natural systems at both local and regional levels. @JASEM

INTRODUCTION

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 and redfish, could contain very high mercury (Hg) levels that they should not be sold to the public based on fish consumption standards set by the US Food and Drug Administration (FDA). 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, water bodies in and around national parks 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. However, Hg levels in different environmental compartments in these parks remain unknown, despite the fact that they do host over five million visitors each year including people who come to camp and fish in these park waters. It is likely that Hg reaching the Gulf Coast park units could result in fish Hg levels that are above safe limits for human consumption, and therefore, lead to human exposure if the park's water bodies have high potentials for MMHg production and accumulation.

Based on field and laboratory investigations, this study was initiated to (1) assess both levels and the extent of Hg contamination, if any, in different environmental compartments of selected park units within the Gulf Islands National Seashore Park Network; and (2) to determine the potential of sediments in these park units to produce and accumulate MMHg.

MATERIAL AND METHODS

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Study site—this study focused on selected islands that are part of the Gulf Islands National Seashore. The study area extends from Florida to Mississippi in southeastern USA, and selected sampling sites included Fort Pickens (FP) on Santa Rosa Island, Naval Live Oaks Park (NLO), and Peridido Key (PK) in Florida (Fig. 1a). In Mississippi, samples were collected from Petit Bois, Horn, East Ship, and West Ship islands (Fig. 1b). Water, sediment, and biota samples were collected during both dry and rainy seasons in Florida, and only during the wet season in park units located in Mississippi.

Sample collection and analytical techniques—surface water samples were collected in acid pre-cleaned Teflon® bottle with gloved hands, using "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 ^{0}C until analysis. Only non-filtered samples were analyzed in this study. Total-Hg (THg) concentrations were determined in water samples after cold oxidation by bromine monochloride (BrCl) prior to reduction with $SnCl_2$. Only labile MMHg was determined on aqueous samples by direct ethylation of non-distilled water sample using sodium tetraethylborate (Bloom, 1989 and references therein).

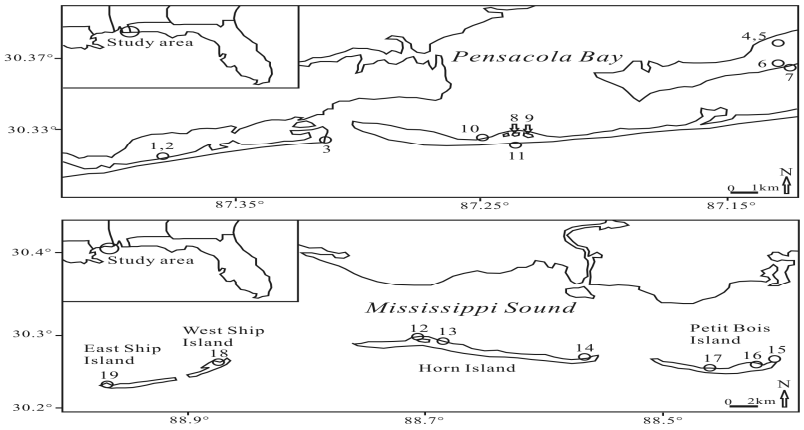

Figure 1: Map showing the location of selected national park units and sampling sites in (*top figure*) the state of Florida, and (*bottom figure*) in Mississippi, USA

For MMHg analysis, the standard addition method was used to account for matrix interferences. Following the ethylation process, MMHg 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 ^{0}C by cold vapor atomic fluorescence spectrometry (CV-AFS). QA/QC procedures included the use of standard addition method, duplicate analyses, reagent blanks and instrument calibration using standard solutions. Details on several aspects on these analytical procedures have been described in our previous publications (e.g., Warner et al., 2003, 2005; Donkor et al., 2005).

Collection and analysis of sediment samples and aquatic plant tissues—sediment samples were collected from all sampling sites by hand coring while seaweeds were grabbed from ocean floor at near shore locations with gloved hands. The latter were from the Ulvaceae family, namely *Ulva prolifera*. Collected samples were placed into acid-cleaned polyethylene re-sealable bags and kept in the dark on ice in coolers until return to the laboratory. THg in these solid samples (i.e. sediment and plant tissues) was determined on wet samples after hot acid digestion with concentrated

HNO_3/H_2SO_4 mixture of a pre-weighed sample (~1g) in acid-cleaned and marble capped volumetric flasks, 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 traps prior to detection by atomic fluorescence spectrometry. MMHg in sediment and plant tissues was determined following an alkaline alcohol (KOH/CH_3OH) digestion of ~1g of wet sediment in an acid-cleaned screw capped Teflon vials and heating at 75^0C. This step was then followed by aqueous ethylation of an aliquot of buffered digestate and MMHg determined as described earlier for water samples. For both MMHg 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 MMHg) was run with all digestions/analyses. The percent recovery on the IAEA-405 averaged 95 ± 11% (*n=10*), and 93 ± 8% (*n=10*) for THg and MMHg, 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 loss on ignition (LOI) as proxy for organic matter content.

Laboratory determination of potential rates of Hg methylation (M) and MMHg degradation (D) in surface sediments—the determination of potential rates of Hg methylation and MMHg degradation were conducted through laboratory assays following a method adapted from Warner et al. (2003). Sediments from each sampling site were mixed with the corresponding in situ water (1:1; vol/vol), homogenized, and apportioned into replicate centrifuge tubes (2-3 mL sediment in 45-mL tubes). Slurries were then bubbled for 1 hour with ultra high purity (UHP) N_2 to accelerate the development of anaerobic conditions and stimulate Hg biotransformation. Individual tubes were dosed with either $HgCl_2$ (for methylation experiments) or CH_3HgCl (for MMHg demethylation experiments) to final concentrations of 1 and 0.010 ppm, respectively. Slurry containing tubes were then incubated statically for 5 days at room temperature (~22˚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 determined ratios of potential transformation rates (M/D ratios) were then used as a parameter to assess the ability of each of the studied sites to produce and ultimately accumulate MMHg.

RESULTS AND DISCUSSION

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 1. 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, Figure 2 gives a comparative view of levels and trends of THg in water (2a) and sediments (2b) during both the dry and rainy seasons. Overall, the obtained results show that THg concentrations in these aquatic systems range from 0.19 ng/L to 14.26 ng/L (Table 1) in the dry season and from 0.71 ng/L to 4.67 ng/L in the rainy season. THg values in about 69% of the analyzed samples fell within the range of previously reported worldwide background concentrations of 0.1 to 3.5 ng/L (Lyons et al., 1999). In contrast, the few samples with measured concentration >5ng/L in this study could be an indication of potential contamination from diffuse sources.

Table 1: THg and MMHg levels in water samples collected from Peridido Key (PK), Fort Picken (FP), Naval Live Oak island (NLO) during the dry season. Italicized numbers in parentheses correspond to sampling site numbers on Fig. 1. (**P = ponds or small lakes; S = sea water*).

			Dry Season	
Sample ID			THg (ng/L)	MMHg (ng Hg/ L)
PK1	*(1)*		3.56	<0.5**
PK2	*(2)*		2.92	<0.5
PK3	*(3)*		2.63	<0.5
NLO-4	*(4)*		1.18	0.7
NLO-5	*(5)*	*P*	0.2	<0.5
NLO-6	*(6)*		10.46	<0.5
NLO-7	*(7)*	*S*	5.64	<0.5
FP1	*(8)*	*P*	14.26	<0.5
FP2	*(9)*	*P*	0.19	<0.5
FP10	*(10)*		6.57	<0.5
FP11	*(11)*		4.29	<0.5
n			*11*	*11*
range			*0.19 - 14.26*	*<0.5 - 0.7*
mean			*4.72*	-

Numbers in parentheses are sampling site ID as shown in Fig. 1 Values below the analytical detection limit.*

Table 2: THg and MMHg levels in water sample collected from PK, NLO, FP and Petit Bois Island (PB) in August, 2004. Italicized numbers in parentheses correspond to sampling site numbers on Fig. 1 and 2. (*P = pond; S = sea water*).

			Wet season	
Sample ID			THg (ng/L)	MMHg (ng Hg/L)
PK1	*(1)*		2.49	<0.50**
NLO	*(6)*	*P*	1.76	<0.50
NLO	*(7)*	*S*	2.48	0.56
FP1	*(8)*	*P*	0.71	<0.50
FP2	*(9)*	*P*	n.d.*	n.d.*
FP10	*(10)*		2.46	<0.50
FP11	*(11)*		0.62	0.61
Horn big lagoon	*(12)*	*P*	3.24	1.02
Horn big lagoon	*(12)*	*S*	3.55	<0.50
Horn ranger	*(13)*	*P*	4.21	<0.50
Horn ranger	*(13)*	*S*	n.d.*	n.d.*
Horn garden	*(14)*	*P*	2.98	<0.50
Horn garden	*(14)*	*S*	2.38	0.61
Petit Bois	*(15)*	*P*	3.58	1.04
Petit Bois	*(15)*	*S*	2.64	0.66
Petit Bois westpond	*(16)*	*P*	0.57	<0.50

Petit Bois westpond	*(16) S*	1.77	<0.50
Petit Bois inland	*(17) P*	0.75	<0.50
Petit Bois	*(17) S*	0.88	<0.50
Westship Island	*(18) P*	0.75	<0.50
Westship Island	*(18) S*	2.08	<0.50
Eastship Island	*(19) P*	4.67	1.58
Eastship Island	*(19) S*	3.11	0.89
n		*21*	*21*
range		*0.57-4.67*	*<0.5-1.58*
mean		*2.27*	-
median		*2.46*	-

**n.d. = not determined; **Values below the analytical detection limit*

Comparatively, THg concentrations in samples collected during the dry season were higher than those measured in the wet season (Fig. 2). 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 (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. In an earlier study, Lewis et al. (2002) reported THg concentrations as high as 70 ng/L in water samples collected from reference and impacted sites near Santa Rosa Sound in Florida. Their high values point to a clear sign of contamination, which we did not see during our sampling campaigns. Unfortunately, the above-mentioned reference does not give necessary information on the sampling, storage, and the handling of their samples.

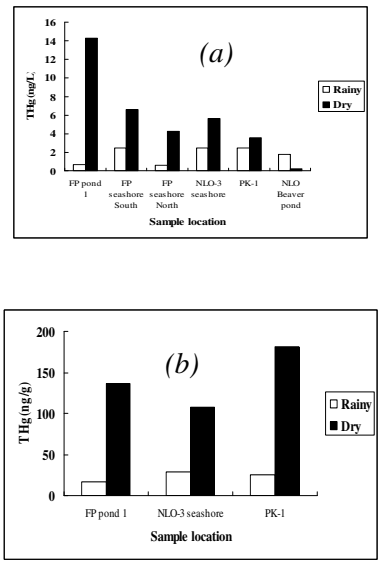

Fig 2: Total-Hg (THg) concentrations in water (a) and sediment (b) samples collected from sites sampled during both the rainy and dry seasons.

In contrast to THg concentrations which varied among sites, MMHg levels differed very little with a good number of measured values at or below the analytical detection limit of 0.5 ng/L to a maximum of 1.58 ng/L (Tables 1 and 2). Overall, these Hg

concentrations are similar to levels reported in the literature for other Southeastern USA aquatic systems with no known direct Hg inputs (e.g., Warner et al. 2005). No correlation was found between THg and MMHg, suggesting that the amount of MMHg in water did not depend on total amount of Hg present in the system. Also, since a significant fraction of MMHg observed in water comes from bottom sediment which is the primary site for MMHg production in most aquatic systems, the observed low MMHg levels are therefore an indication of probable low Hg methylation potentials or low M/D ratios in studied aquatic systems. Data obtained from laboratory experiments and presented later herein support this explanation.

The literature is quite abundant with Hg data determined in coastal aquatic environments worldwide. Table 3 summarizes some of the published Hg data on coastal waters and sediments. Based on this data compilation, the aquatic systems located in the Gulf Islands National Seashore fall on the low to mid-range of the tabulated values compared. In this table, sites with excessively high values are those with known Hg point sources associated with well-identified anthropogenic activities. However, and as seen in Table 3, most published papers report only THg values while papers on the investigation of both THg and MMHg concentrations remain very limited.

Mercury levels and speciation in sediments: concentrations of THg and MMHg determined on non-sieved wet sediment samples ranged from 29 to 838 ng/g, and 1 to 17 ng/g, respectively. Corresponding data are presented in tables 4 and 5. 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 is observed. The distribution of THg data followed the structural pattern of sediments (based on visual observations), 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. Finally, the organic matter (OM) content in sediments was found to be a significant and positive function of sediment THg (r^2=0.84; $p<0.05$).

Table 3: Total (THg) and methyl (MMHg) mercury data for selected coastal waters and sediments collected from locations with and without known sources of Hg pollution. Data from this study are listed as "Gulf of Mexico"

Coastal Sites with recently reported THg	Water (ng/L)		Sediment (ng/g)		References
and MMHg data	THg	MMHg	THg	MMHg	
Coastal lagoon, Rio de Janeiro (Brazil)	3.64 - 11.04		120 - 440		*Lacerda and GonÇalves, 2001*
Coastal lagoon (Ria de Aveiro, Portugal)**	1 - 275.4		100 – 51,700		*Coelho te al., 2005*
Eastern Lebanese sea (Lebanon)	0.31 - 0.44				*Nakhlé et al., 2006*
The North Sea	0.18 - 0.96				*Coquery and Cossa, 1995*
South Florida Estuaries (USA)	3 - 7.4	BDL - 2.3	1 - 219	BDL - 0.49	*Kannan et al., 1998*
Ulhas estuary (India)**	40 – 610		80~190		*Ram et al., 2003*
North shore of Long Island (USA)**			71.1 – 5,250		*Goldblum et al., 2006*
Baltic sea (Poland)			37 - 880	0.01 - 2	*Kannan and Falandysz, 1998*

South China Sea (Malaysia)			20 - 127	0.01 - 0.053	*Kannan and Falandysz, 1998*
Coastal Bering Sea (Russia)			77 - 112	0.1 - 0.62	*Kannan and Falandysz, 1998*
Portuguese coast (Spain)			BDL - 870		*Coelho et al., 2006*
Bay of Fundy (Canada)			7 - 79		*Hung and Chmura, 2006*
Kastela Bay (Croatia)**	69 – 145		14,280 – 74,000	6.05 - 36.74	*Kwokal et al., 2002*
Scheldt estuary (Belgium)	1.5	0.12	900	3.4	*Bayens et al., 2003*
Gulf of Trieste (Italy)**	50	0.2	38.4	2.9	*Hines et al., 2000*
Barrier islands, Gulf of Mexico (USA)	0.19 - 14.26	<0.5 - 1.58	6.4 - 838	1~17	*Youn et al., (this study)*

** *Study sites with known point sources of Hg pollution*

The highest concentrations of MMHg were measured in samples collected from Fort Pickens pond (12 ng/g) for Florida, and Petit Bois (17 ng/g) in Mississippi. 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 MMHg in these sites (Gilmour et al., 1992; Bloom, 1989). When compared to MMHg data sets that are available in the peer reviewed literature, some of the numbers obtained in this study do largely exceed MMHg values reported from most aquatic systems with no known point sources of Hg (0.01-7.8 ng/g) (e.g. Warner et al., 2005). These MMHg data will be discussed further in relation with the ability of these sediments to produce and accumulate MMHg based on our laboratory methylation and demethylation assays.

Mercury levels in plant tissues— Some of the sites sampled during this study provide a variety of habitats suitable for the growth of benthic marine algae. The most common species to these sites, *Ulva prolifera,* was collected from 7 sites during the wet season only, and the determined THg concentrations ranged from 105.9 to 237.1ng/g on wet weight basis (Table 6).

Table 4: THg and MMHg levels (ng as Hg/g of wet sediments) in surface sediment samples collected from PK, FP, NLO in March, 2004. Italicized numbers in parentheses correspond to sampling site numbers on Fig. 1 and 2. (*P = pond; S = sea water*).

		Dry Season		
Sample ID		THg (ng/g)	% water	LOI (% OM)
PK1	*(1)*	181	50.19	5.43
PK1'	*(1)*	213	48.27	4.51
PK2	*(2)*	558	74.62	38.99
PK3 (marsh)	*(3)*	115	25.98	0.9
PK3 (marsh)	*(3)*	29	51.86	4.54
NLO4	*(4)*	418	81.43	48.39
NLO5	*(5)*	203	44.88	7.78
NLO6	*(6) P*	838	85.54	71.17
NLO7	*(7) S*	108	35.73	18.79
FP1	*(8) P*	136	39.81	4.93
FP2	*(9) P*	56	49.78	4.05

n	*11*	*11*	*11*
range	*29-838*	*25.98-*	*0.9-71.17*
mean	*259.55*	*53.46*	*19.04*
median	*181*	*49.78*	*5.43*

Measured THg concentrations were lower than values reported for most aquatic plants collected from salt marshes. For example, THg levels in coastal wetland plants analyzed by Windham et al. (2003) ranged from 332.8 to 840ng/g. In contrast, in non-polluted coastal water bodies, Lewis et al. (2004) measured THg concentrations that were much lower (31 to 50 ng/g) than those determined in this study. Owing to the restrictive root mechanism, Hg in plants could tend to concentrate in roots (Greger et al., 2005). Windham et al. (2003) found that 70 to100% of the metal concentration of a whole plant was contained in the roots. Accordingly, this preliminary investigation needs to be followed by a well-designed study to look at both Hg speciation in aquatic plants and Hg levels in higher trophic level organisms. Finally, the lack of relationship between THg levels in analyzed plant tissues and THg in either sediments or water could simply be due to the fact THg is not necessarily equal to the bioavailable Hg fraction in water or sediments.

Potential rates of Hg methylation and MMHg demethylation—determined potential rates of Hg methylation (M), and MMHg demethylation (D) as well as calculated M/D ratios are given in Table 7. Potential rates of MMHg demethylation ranged from zero to 9.07 ng g^{-1} day^{-1} and potential rates of Hg methylation ranged from 0 to 42.90 ng g^{-1} day^{-1}. M/D ratios have been widely used to compare the relative rates of Hg biotransformation from different environment types (Warner et al., 2003). M/D ratios determined in this study ranged from zero when no Hg methylation was observed to a value of 6.765. However, the majority of sites had M/D ratios <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 MMHg concentrations as they represent the net balance of the co-occurring processes of Hg methylation and MMHg demethylation.

Table 5: THg and MMHg levels (ng as Hg/g of wet sediments) in surface sediment samples collected during the wet season. Italicized numbers in parentheses correspond to sampling site numbers on Fig. 1 and 2. (*P = pond; S = sea water*)

		Wet Season			
Sample ID		THg (ng/g)	MMHg (ng/g)	% water content	% OM
PK1	*(1)*	24.9	1	**n.d*	**n.d*
NLO7	*(7) S*	28.4	5	*n.d*	*n.d*
FP1	*(8) P*	16.4	12	*n.d*	*n.d*
FP seashore South	*(10)*	11.8	3.3	*n.d*	*n.d*
FP seashore North	*(11)*	11.6	1	*n.d*	*n.d*
Horn big lagoon	*(12) P*	12.1	3.7	20.61	0.82
Horn big lagoon	*(12) S*	7.8	3	19.75	0.35

Horn Ranger	*(13) P*	26.7	1.2	19.59	20.05
Horn Ranger	*(13) S*	10.4	1	0.5	0.38
Horn garden	*(14) P*	20.2	2.3	48.9	3.08
Horn garden	*(14) S*	11.7	3	19.62	0.49
Petit Bois lagoon	*(15) P*	10.3	3.1	32.31	2.6
Petit Bois lagoon	*(15) S*	11.7	6.1	20.39	0.36
Petit Bois west	*(16) P*	25.8	17	37.57	3.73
Petit Bois west	*(16) S*	9.3	4.2	20.98	0.41
Petit Bois inland	*(17) P*	6.4	4.9	48.19	3.36
Petit Bois inland	*(17) S*	11	1	24.25	0.32
Westship Island	*(18) P*	89.2	1	32.77	1.94
Westship Island	*(18) S*	8.3	1	22.56	0.4
Eastship Island	*(19) P*	34.6	1	67.3	16.33
Eastship Island	*(19) S*	28.8	2.3	23.51	3.55
n		*21*	*21*	*16*	*16*
Range		*6.4-89.2*	*1-17*	*0.5-67.3*	*0.32-20.05*
mean		*19.88*	*3.72*	*28.68*	*3.64*
median		*11.80*	*3.00*	*23.04*	*1.38*

**n.d: not determined*

Our experimentally generated M/D ratios did not correlate well with sediment ambient MMHg concentrations. This observation points out the complexity of factors controlling the net product of M and D, which are still poorly understood. For instance, some of the sediment used in this study had a very strong smell characteristic of H_2S, a potential indication of active sulfate reduction which can limit Hg bioavalability to methylating microorganisms via formation of insoluble HgS complexes (Ullrich et al., 2001). In addition, the sediment organic matter content which tends to enhance methylation rates was quite low in most of these sediment samples (Table 5).

Table 6: Total mercury (THg) concentrations in nanograms per gram (ppb) of wet plant tissues (*Ulva prolifera*) collected from 7 seashore sites in Mississippi's park.

Sampling sites ID		Total-Hg (ng/g wet weight) in aquatic plant tissues
Horn big lagoon	*(12)**	172.01
Horn garden	*(14)*	111.90
Petit Bois-lagoon	*(15)*	237.10
Petit Bois-westpond	*(16)*	199.70
Petit Bois-inland	*(17)*	153.90
Eastship Island	*(18)*	105.90
Westship Island	*(19)*	196.80

**Numbers in parentheses indicate sampling site as shown in Fig.1*

Overall, it is rather obvious that available experimental approaches used in the determination of potential rates of Hg transformations have one common drawback, the lack of the ability to mimic the speciation and bioavailability of ambient sedimentary Hg, and the addition of rather large amounts of Hg salts to sediments with initially low available Hg could alter the sediment response. Ideally, the most recent techniques for measurements of potential Hg methylation rates in sediments with low ambient THg levels that rely on the use of trace stable isotopes of Hg should be used (e.g. Rodriguez et al., 2004). However, the use of such stable isotopes to study mercury transformations in natural systems is very expensive.

The use of only 0.01 mg of Hg added as CH_3HgCl per kg of sediments resulted in much higher potential rates of MMHg demethylation. One probable explanation to these high D values is that the demethylation process is less dependent upon aerobic and anaerobic conditions, and more dependent upon high pH (>7) common to these investigated systems (Matilainen et al., 1991). Nevertheless, based on obtained data, it is likely that the production and accumulation of MMHg should be very limited in these systems and our experimental data support most of the observed low ambient MMHg 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 MMHg levels in sediments (Kannan et al., 1998; 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 MMHg to biota.

Table 7: Potential rates of Hg methylation (M) and MMHg demethylation (D) and M/D ratios. (*No numbers are shown for samples with zero potential for either Hg methylation or MMHg demethylation; P = pond; S = saline sea water*)

Sampling sites		Potential rates of methylation (M) (ng/g/day)	Potential rates of demethylation (D) (ng/g/day)	$\frac{M}{D}$ ratios
PK1	*(1)*	0.30	33.48	0.009
PK1'	*(1)*	4.61	33.54	0.137
PK2	*(2)*	0.60	6.47	0.093
PK3 (marsh)	*(3)*	1.27	6.37	0.199
PK3 (marsh)	*(3)*	1.07	42.90	0.025
NLO4	*(4)*	0.76	10.92	0.070
NLO5	*(5)*	0.90	11.40	0.079
NLO6	*(6) P*	-	7.49	-
NLO7	*(7) S*	0.36	-	-
FP1	*(8) P*	0.10	14.00	0.007
FP2	*(9) P*	nd	13.74	-
Horn big lagoon	*(12) P*	9.07	3.87	2.344
Horn big lagoon	*(12) S*	8.93	1.32	6.765
Horn ranger	*(13) P*	7.12	2.79	2.552

Horn ranger	*(13) S*	7.08	-	-
Horn garden	*(14) P*	5.41	6.18	0.875
Horn garden	*(14) S*	5.88	4.37	1.346
Petit Bois lagoon	*(15) P*	5.98	-	-
Petit Bois lagoon	*(15) S*	6.52	-	-
Petit Bois West	*(16) P*	4.64	21.94	0.211
Petit Bois West	*(16) S*	5.46	8.44	0.647
Petit Bois	*(17) P*	1.38	9.82	0.141
Petit Bois	*(17) S*	8.55	-	-
Eastship Island	*(18) P*	1.96	14.50	0.135

Conclusion: This preliminary examination of Hg levels and speciation in different environmental compartments of the Gulf Islands National Seashore in southeastern USA has shown that water, sediments, and aquatic plants in these parks have relatively low THg and MMHg and can be considered mostly non-polluted based on both background values reported in the literature and 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 several site specific conditions. Based on data obtained in this study, one could speculate that the ability of sampled sediments to produce and accumulate MMHg should be low. However, and as stated above, the complexity of Hg bioaccumulation and biomagnification in aquatic food chains may not support the above conclusion, and an investigation of Hg levels in fish and shellfish is probably the only effective way to address the issue of fish contamination in these systems.

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