Appendix 7-12: Florida Bay Mercury Screening Study

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INTRODUCTION

In the Everglades Forever Act (EFA; Ch. 373.4592, F.S), the Legislature recognized that improved water supply and hydroperiod management were crucial elements to overall revitalization of the Everglades ecosystem, including Florida Bay. To meet this management object the District has constructed and is currently testing the S-332D pump, with the eventual goal of implementing its operation as part of the C-111 and Modified Water Deliveries projects. The primary purpose for the pump station is to increase surface water flows to Florida Bay via Taylor Slough. With the EFA, the Legislature also recognized that the Everglades ecosystem must be restored both in terms of water quantity and water quality and must be preserved and protected in a manner that is long-term and comprehensive.

BACKGROUND

Fish surveys in Taylor Slough and eastern Florida Bay conducted by both the Florida Game and Fresh Water Fish Commission (FGFWFC) and the Florida Department of Environmental Protection (FDEP) in the late 1980s and early 1990s routinely found mercury concentrations exceeding 1.0 ppm (T. Lange, personal communication; Strom and Graves, 1995). In 1995, the FDEP, the Department of Health and Rehabilitative Services and the Everglades National Park jointly issued a health advisory recommending limited-consumption of upper trophic level fish in Florida Bay due to elevated levels of mercury. More recent surveys of mercury in fish from Florida Bay report concentrations up to 0.78 ppm wet weight (3.9 ppm dry weight; Kannan et al., 1998). Likewise, oysters (*Crassostrea virginica*) monitored at sites in south Florida under the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Project (Cantillo et al., 1997), have consistently shown highest mercury concentrations at Joe Bay, which is the main flow path for surface water to eastern Florida Bay. In an ongoing study, other NOAA researchers report tissue concentrations in spotted seatrout (*Cynoscion nebulosus*) from eastern Florida Bay routinely exceed 0.5 ppm wet weight, which is the criterion for limited consumption (Evans & Engel, 1999). Moreover, mercury also appears to be bioaccumulating in fish-eating birds that forage in the Bay. A study of sick or injured birds at the Florida Keys Wild Bird Center found concentrations of up to 250 ppm mercury in livers of double-crested cormorants (Sepulveda et al., 1998). These levels are three times higher than liver concentrations reported for great blue herons from the Everglades (Sundlof et al., 1994).

Nonetheless, at present, little is known about the sources of mercury contamination to Florida Bay. Only two small-scale studies have been conducted to investigate mercury in surface water flows from the mainland. Kannan et al. (1998) reported high concentrations of both total mercury and methylmercury (3-7.4 ng/L and <0.002-2.3 ng/L, respectively) in filtered water samples collected from canals and creeks flowing into eastern Florida Bay. A follow-up study by the U.S. Environmental Protection Agency (EPA) reported methylmercury in filtered samples from these same creeks at concentrations up to 0.395 ng/L during the wet season and up to 0.575 ng/L in the dry season (Lores et al., 1998). Results from these limited studies suggest that surface water flows from the mainland may make a significant contribution of total mercury and methylmercury to eastern Florida Bay. If this is the case then increased surface water deliveries to eastern Florida Bay via Taylor River could worsen the mercury problem by increasing methylmercury loading. Yet, data from the Florida Atmospheric Mercury Study (FAMS), which consisted of collection sites across the state including sites at the Beard Research Center and on Little Crawl Key, clearly shows atmospheric deposition is the primary source of inorganic mercury to south Florida (Guentzel et al., 1995). Therefore, it is also equally plausible that atmospheric loading of inorganic mercury accounts for the observed mercury contamination in Bay. However, the significance of atmospheric loading to methylmercury bioaccumulation in Bay fish is dependent on the rate of *in situ* methylation. If *in situ* methylation, which can be spatially highly variable depending on a number of factors, is low then the relative importance of methylmercury loading from the mainland increases. However, increased surface water deliveries from the mainland and attendant changes in porewater chemistry (e.g., salinity, redox conditions, and sulfide concentrations) has the potential to also alter the rate of *in situ* methylation in the Bay.

Accordingly, in 2000, the District initiated a one-year scoping-level study to establish baseline data on seasonal mercury loading and methylmercury bioaccumulation in eastern Florida Bay. This baseline data will be critical to determine if the increased diversion of Everglades' fresh water through Taylor Slough will worsen the mercury contamination problem in Eastern Florida Bay. Results from this study will support informed Everglades restoration decision making during various phases of the C-111 and Modified Water Deliveries projects and in the future during the Comprehensive Everglades Restoration Plan (CERP). This document reports results from the initial sampling event that occurred during February–March 2000.

STUDY SITE AND METHODS

Florida Bay is a large (1800 square km), shallow (<2 m), estuarine system located at the southern tip of the Florida Everglades. Fresh water flow through the Everglades and into Florida Bay is a key avenue by which these two ecosystems interact. On February 28 – March 7, 2000, samples were collected along two transects into Florida Bay (see **Figure A7-12-1**) under appropriate state and federal permits (E-00-08 and 1999132, respectively). The first transect follows the current flow path into eastern Florida Bay and begins in the C111 basin, extends south down into Joe Bay, and out through Trout Creek into the Bay. The second transect follows the flow path of Taylor Slough, which is expected to experience increased flows with efforts associated with the C-111 and Modified Water Deliveries projects, out through Little Madeira Bay into the Bay. In

addition, one site in western Florida Bay was sampled as a reference site. Efforts were made to co-locate these sites with existing water quality monitoring sites.

Surface water, sediment and fish were collected using methods adapted from standard operating procedures developed for the Everglades Mercury Screening Program (SFWMD-Hg-SOP10: Mercury in Surface Water, SFWMD-Hg-SOP04: Mercury in Fish and Macroinvertebrates, SFWMD-Hg-SOP08: Mercury in Sediment). Briefly, employing a clean hands – dirty hands technique, duplicate samples of both filtered and unfiltered surface water were collected from mid-depth using a peristaltic pump and ultra-cleaned Teflon sampling train. Samples were immediately shipped to a contract-laboratory for determination of total mercury (THg), total dissolved mercury (THgF), mono methylmercury (MMHg) and dissolved mono methylmercury (MMHgF). Dissolved species were operationally defined as material passing through a 0.45 µm Meissner capsule filter. Four sediment cores (4 cm depth) were collected at each location using clean Butyrate core tubes, composited to form a single sample, homogenized and analyzed for both THg and MMHg (based on dry weight). At each location attempts were also made to collect representative small-size bait fish species, medium-size prey fish species and large-bodied predatory fish species. Small-size bait fish species (fresh and marine; mosquitofish, *Gambusia* spp.; sailfin molly, *Poecilia latipinna*; rainwater killifish, *Lucania parva*; anchovies, *Anchoa mitchilli*, killifishes, *Fundulis* spp.; sheepshead minnow, *Cyprinodon variegatus*; silversides, *Menidia* spp.) were collected using long-handled dip nets, cast nets (1/4 in mesh size) and/or throw traps (species varied along the gradient). Small baitfish (n = approximately 100) were pooled by species, homogenized and treated as a composite sample from each site. Medium-size prey fish species (fresh and marine; mayan ciclid, *Cichlasoma urpophthalmus*; sunfish, *Lepomis* spp.; mojarra, *Eucinostomus* spp.; silversides, *Menidia* spp.; mullet, *Mugil* spp.; pinfish, Lagodon rhomboides; pigfish, *Orthopristis chrysoptera*, spottail pinfish, *Diplodus holbrooki*, false pilchard, *Harengula clupeola*, Atlantic thread herring, *Opisthonema oglinum*) were collected in replicate (n=5) by cast net or hook-and-line. Whole fish were then homogenized (i.e., with stomach contents) using a commercial meat grinder or food processor with stainless steel blades. At each site attempts were also made to collect large-bodied predatory fish species, including gamefish (fresh and marine; largemouth bass, *Micropterus salmoides*; spotted seatrout, *Cynoscion nebulosus*; redfish, *Sciaenops ocellatus*; gray snapper, *Lutjanus griseus*; Jack Crevalle, *Caranx hippo*; Gafftopsail catfish, *Bagre marinus*; common snook, *Centropomus undecimalis;* flounder, *Paralichthys* spp.) in replicate (n=5) by hook-and-line. Fillets of these fish were then analyzed for total mercury. Because more than 95 percent of the THg in fish is MMHg (Grieb et al., 1990; Watras, 1993), analysis of fish tissue for THg is interpreted as equivalent to the analysis of fish tissue for MeHg for the purposes of this report.

Additionally, temperature, conductivity, salinity, turbidity and dissolved oxygen were measured at a minimum of three depths (0.5 m from the bottom, mid-depth and 0.5 m from the surface) at each location using a YSI 6920 Multi-parameter water quality monitor.

Surface water samples were analyzed for THg and MMHg and sediments analyzed for MMHg by Frontier Geosciences of Seattle, WA. THg analysis was carried out using EPA Method 1631 (EPA-821-R-99-005). In brief, all mercury in the sample was oxidized to Hg(II) using 0.2N bromine monochloride solution. After oxidation,

hydroxylamine hydrochloride was added to inhibit further reaction and to destroy free halogens. Hg(II) was reduced to volatile Hg(0) by the addition of stannous chloride. The Hg(0) was then separated from solution by purging with nitrogen and concentration onto a gold-coated sand trap. The trapped Hg was thermally desorbed from the gold trap and determined using cold vapor atomic fluorescence spectroscopy. Following codistillation into pure water, MMHg was determined by aqueous phase ethylation using sodium tetraethyl borate (sodium tetraethyl borate converts nonvolatile monomethyl Hg to gaseous methyl ethyl Hg), followed by purge-and-trap on a Carobotrap™. The trap was then thermally desorbed into an isothermal GC column for peak separation and then quantified by cold vapor atomic fluorescence spectroscopy (Bloom, 1989).

THg concentrations in fish tissues and sediments were determined by the Florida Department of Environmental Protection (FDEP) Chemistry Laboratory in Tallahassee, Florida using a modified version of EPA Method 245.6. The mercury in the sample was first oxidized to Hg(II) using a combination of potassium permanganate and potassium persulfate. Hydroxylamine hydrochloride was then added to reduce excess oxidizing reagents. The mercuric ions in solution were reduced to Hg(0) using stannous chloride and purged into an atomic absorption spectrometer (Varian SpectraAA 400 with SPS5 autosampler, Mulgrove, Victoria, Australia) using UHP grade nitrogen.

Quality control blanks for surface water, which included trip blanks, field blanks and equipment blanks, were all negative for MeHg. Alternatively, ultratrace levels of THg (< 0.41 ng/L) were detected in two trip blanks and two of the four equipment blanks. However, all values were less than 2 times the method detection limit plus background concentration of THg in Milli-Q water supplied as blank water (0.094 ng/L). Thus, field data were not invalidated. Relative percent differences (RPD) between field duplicates were <13.3% and <15.14% for THg in unfiltered and filtered water samples, respectively. RPDs between field duplicates were <6.6% and < 8.9% for MMHg in unfiltered and filtered water samples. Laboratory quality control samples for the analyses of water included laboratory fortified blanks, matrix spikes, matrix spike duplicates, lab duplicates and Standard Reference Materials (SRMs). Recoveries for lab fortified blanks averaged 102 % (n=3) for THg and 93.9 % (n=4) for MeHg for sample batches of surface water. Recovery in lab fortified blanks was 98.7% for THg (n=2) and 107% for MMHg (n=1) during sediment analyses and 100.1% for THg (n=8) during tissue analyses. Matrix spike recovery of THg in field collected water were all within the range of 75-125%, averaging 94.4% (n = 6). Matrix spike recovery of MMHg in field collected water was slightly more variable, ranging from 132.4 to 99.5% (n=3, mean was 112%). Matrix spike recovery of THg in fish were all within the range of 75- 125%, and averaged 101.3% (n=14). Matrix spike recoveries in sediment averaged 88.7% (n=2) for THg and 79.3% (n=1) for MeHg. RPDs between laboratory duplicates (all matrixes) were <18.0 % for MeHg (n=4) and <16.4% for THg (n=16). Recoveries in SRMs averaged 95.7 % (n=5) for MeHg and 94.9% (n=4) for THg. Method detection limits (MDLs) were 0.18 ng/L for THg in water and 0.021 ng/L for MeHg in water. MDLs for THg in fish tissues ranged from 6.4 to 8.3 ng/g in small baitfish and 19 to 21 ng/g for other fish. MDLs were 0.003 ng/g for MeHg, and ranged from 8.4 to 22 ng/g for THg in sediments.

RESULTS

Concentrations of THg in surface water ranged from 0.43 to 1.51 ng/L in unfiltered samples and from 0.26 to 1.35 ng/L in filtered samples (THgF). Concentrations of MMHg in surface water ranged from <0.025 to 0.3 ng/L in unfiltered samples and from <0.021 to 0.259 ng/L in filtered samples (MMHgF). All mercury species were at maximums in the transition zone at the mouths of Taylor River (Site 4) and the creek flowing into Joe Bay (Site 10) and decreased both upstream and downstream along the north-south transects (**Figure A7-12-1**). MMHg fell to near detection or below detectable levels in unfiltered and filtered samples at both ends of the transects.

Dissolved THg dominated over particle-bound mercury at most sites (estimated by difference, THg less THg filtered), particularly at the mouths of Taylor River and the inflow to Joe Bay (**Figure A7-12-1**); however, particle-bound THg was a significant fraction of THg at the reference site. While dissolved MMHg also dominated over particle-bound MMHg at inflows, fractionation at other sites was highly variable.

THg and MMHg in sediments from Florida Bay and upstream canals ranged from 9.9 to 63 ng/g and 0.063 to 2.33 ng/g dry weight, respectively. As was the case in surface water, highest sediment-THg concentrations occurred at the mouth of Taylor River and in sediments from the creek flowing into Joe Bay (**Figure A7-12-2**) and decreased both upstream and downstream.

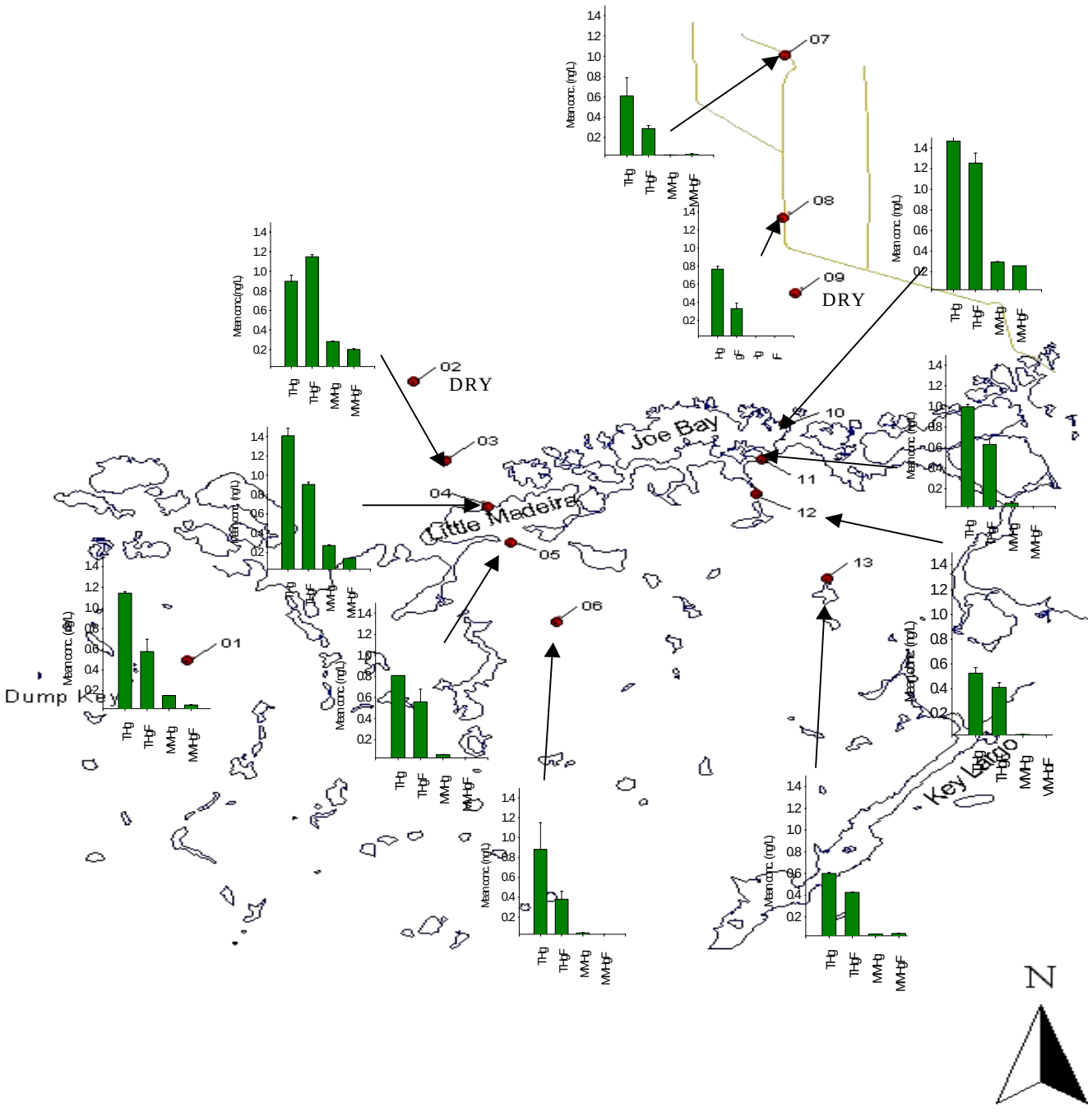

Figure A7-12-1. Spatial trends in mercury in waters of Florida Bay and associated inflows (THg – total mercury, THgF – total mercury filtered, MMHg – mono methylmercury, MMHgF – mono methylmercury filtered).

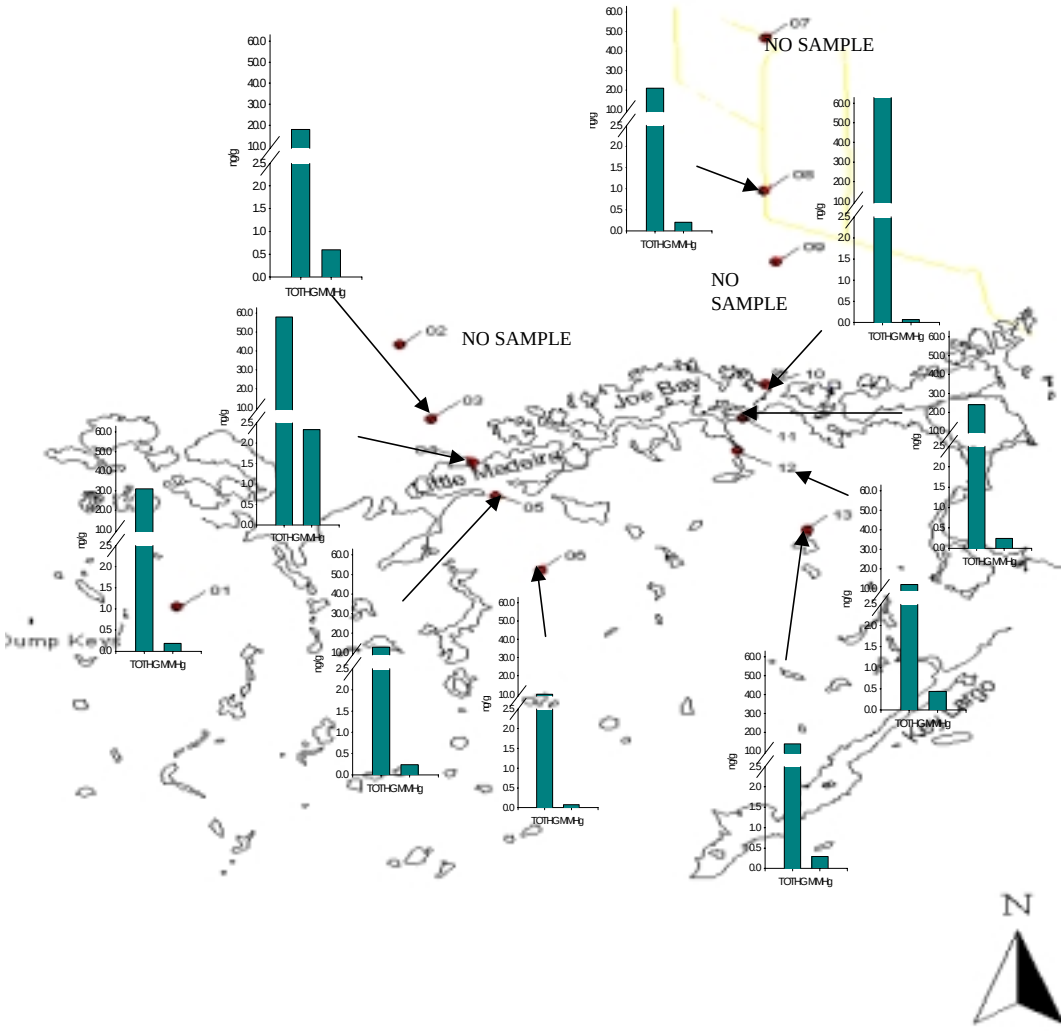

Figure A7-12-2. Spatial trends in mercury in sediment of Florida Bay and upstream canals and creeks (TOTHg – total mercury, MMHg – mono methylmercury).

Maximum concentration of MMHg in sediments also occurred at the mouth of Taylor River; however, MMHg was relatively low in sediments in the creek flowing into Joe Bay. In general, the spatial patterns in sediment-mercury in combination with relative low particle-bound THg concentrations observed in water at Taylor River and in the creek entering Joe Bay suggest particle deposition as freshwater entered Little Madeira and Joe Bay, possibly due to a decrease in current velocity, flocculation of negatively charged particles and a general decrease in solubility.

Small-size baitfish were found and collected at only three sites (Sites 3, 7, and 8). Mercury concentrations in these fishes ranged from 0.043 mg/kg in mosquitofish (*Gambusia spp.*) from Site 7 to 0.207 mg/kg in silversides (*Menidia beryllina*) from Site 3. Concentration of mercury in homogenates of whole medium-size prey fish ranged from 0.047 mg/kg in a bluegill (*Lepomis macrochirus*) from Site 7 to 0.58 mg/kg in an oscar (*Astronotus ocellatus*) from Site 8 (mean ±1SD: 0.32 ±0.15). Concentration of mercury in fillets from large-bodied predatory fish ranged from 0.075 mg/kg in a gafftopsail catfish (*Bagre marinus*) from Site 10 to 1.4 mg/kg in a Jack Crevalle (*Caranx hippos*) from Site 4 (mean ±1SD: 0.472 ±0.30). Spatial patterns of mercury concentrations in fillets of select species (i.e., sample size greater than 2 fish) are shown in **Figure A7-12-3**.

DISCUSSION

With results from only one sampling event it would be premature to speculate on the significance of the observed spatial patterns in mercury concentrations. Although the observed gradients in surface water and sediments (**Figures A7-12-1 and -2**) may implicate runoff from the mainland as a significant source, spatial patterns will likely vary seasonally. Results from future sampling will hopefully provide additional information on spatial gradients and the various factors that produced them. Nevertheless, it is noteworthy that observed concentrations of both THg and MMHg in surface water flowing into Florida Bay were lower than values reported in earlier studies in the region (3-7.4 ng THg/L and <0.002-2.3 ng MMHg/L, Kannan et al., 1998; and 0.395 ng MMHg/L to 0.575 ng MMHg/L, Lores et al., 1998). While concentrations of THg in sediment samples reported here were lower than previous surveys (3–100 ng/g THg), observed maximal MMHg concentrations were higher (<0.001-0.318 ng/g MMHg; Kannan et al., 1998). Concentrations of mercury in fish reported were consistent with levels recently reported by other investigators (Evans and Engel, 1999). However, because of the small sample size that was distributed among a number of different species, here again caution must be exercised when interpreting spatial patterns in the data. Moreover, while 12 fillets from 35 fishes (34%) collected during this first sampling event exceeded the criterion for unlimited consumption (i.e., 0.5 mg/kg), many of the gray snappers were undersized. Consequently, this sampled population may underestimate human health risk from ingesting fish of legally harvestable size from eastern Florida Bay.

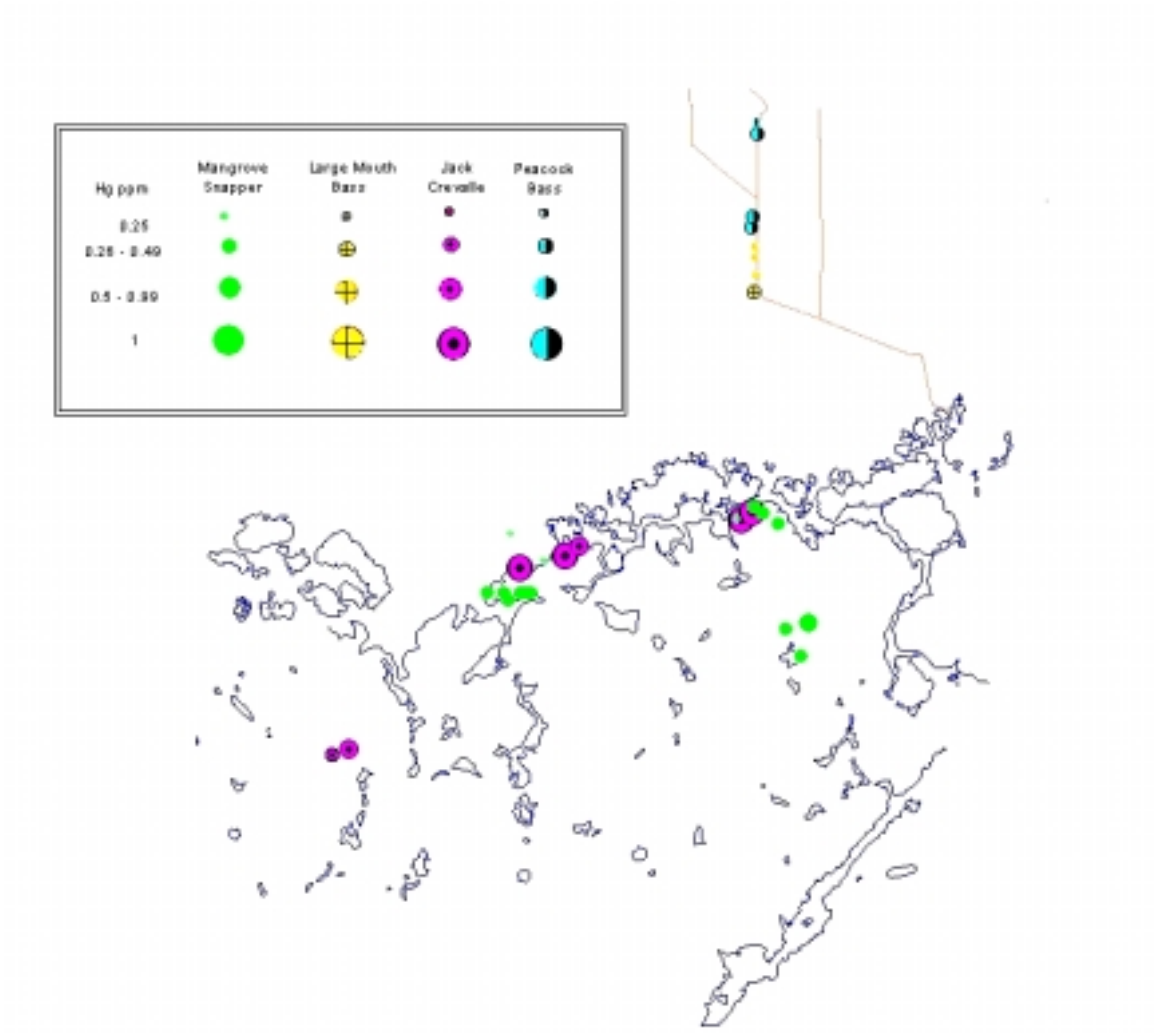

Figure A7-12-3. Spatial patterns of THg concentrations in fillets of select fish species collected in Florida Bay during February – March 2000.

Results from future sampling will be evaluated in terms of THg and MMHg loads delivered to eastern Florida Bay via Joe Bay and Taylor Slough. Using flow data (i.e., from USGS – Eduardo Patino and SFWMD), a mass budget approach will be developed similar to the nutrient mass budget approach employed by Rudnick et al. (1999) in the same region. The ultimate goal is to use existing Florida Bay hydrodynamics and water quality models as inputs to a new Florida Bay mercury transport-fate-bioaccumulation model to provide an accurate scientific assessment of the environmental ramifications from increased or redirected flow. In closing, it should be noted that this monitoring program was recently selected to receive funding support from NOAA's South Florida Ecosystem Restoration Prediction and Modeling Program, as part of a larger two-year collaborative study with NOAA's National Centers for Coastal Ocean Science (Beaufort Laboratory).

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