

# Appendix 4A-4: Annual Permit Compliance Monitoring Report for Mercury in the Stormwater Treatment Areas

Darren Rumbold

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## SUMMARY

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This report summarizes data from compliance monitoring of mercury storage, release, and bioaccumulation in Stormwater Treatment Areas (STAs) during Water Year 2003 (WY2003) (May 1, 2002 through April 30, 2003).

Key findings are as follows:

1. **All STAs:** During the monitoring period, there were no violations of the Florida Class III numerical water quality standard (WQS) of 12 nanograms (ng) of total mercury per liter (THg)/L. As such, the project has met the requirements of Section 6.i of the mercury-monitoring program of the referenced permits. However, the problem form of mercury (Hg) is methylmercury (MeHg), which is produced from inorganic mercury in rain, runoff, and sediments or flooded soils by natural bacteria present in aquatic ecosystems. MeHg is highly toxic and magnifies up the food chain (biomagnifies) to levels that have impaired the Everglades sport fishery. These levels could threaten some sensitive, highly exposed members of some fish-eating wildlife species, including endangered species such as the wood stork and Everglades mink. Florida does not have a separate WQS for MeHg, but the U.S. Environmental Protection Agency (USEPA) has published a water quality criterion of 0.3 parts per million (ppm) (also expressed as mg/kg) THg as MeHg in fish flesh to protect human health.
2. **STA-6:** After five years of operation, STA-6 continued to exhibit fluctuations in Hg species in water. Following a drydown and rewetting event during the second quarter of 2002, concentrations of THg and MeHg in the unfiltered surface water spiked at STA-6 outflows, reaching 8.8 ng THg/L and 6.5 ng MeHg/L, respectively. Resident fishes continued to exhibit a positive percent change in Hg across STA-6; however, there was no evidence of significant increases in mercury bioaccumulation in fishes over baseline following the spike in water column MeHg. Although levels of Hg in STA-6 fishes have fluctuated near baseline and are similar to or lower than levels found in fish from other Everglades areas, fish-eating wildlife feeding preferentially at STA-6 face some risk of adverse chronic effects from mercury exposure, based on U.S. Fish and Wildlife Service (USFWS) and USEPA criteria. However, to date the South Florida Water Management District (SFWMD or District) has not performed a formal assessment of the site-specific risks of MeHg toxic effects to fish-eating

birds and mammals foraging preferentially in STA-6, and none is now planned. Appendix 2B-6 discusses the results of the Mercury Special Studies (MSS) that were initiated to more accurately characterize the anomalous mercury behavior of STA-6.

3. **STA-5:** This location also exhibited spikes in surface water THg concentration following summer rains, yet unlike STA-6, there were no corresponding increases in surface water MeHg. During the reporting year, levels of Hg in mosquitofish from the interior marshes of STA-5 were much lower than peak levels observed in 2000. Despite good-faith efforts of sampling personnel from the Florida Fish and Wildlife Conservation Commission (FWC), few large-bodied fish were caught at STA-5 this year. Consequently, little can be inferred regarding mercury levels in STA-5 sunfish or bass in 2002.
4. **STA-1W:** The Everglades Nutrient Removal (ENR) Project, which served as the prototype STA, was subsumed by STA-1W in April 1999. It continued to have only low concentrations of both THg and MeHg in surface water, consistently showed negative percent change in both THg and MeHg across the STA, and exhibited greatly reduced MeHg bioaccumulation in resident fishes relative to Everglades fishes.
5. **STA-2:** Although THg concentrations did not exceed the Class III water quality standard of 12 ng/L in the outflow of STA-2, both THg and MeHg were consistently at greater concentrations in the outflow as compared to the inflow of this STA. This positive percent change in THg and MeHg across the STA was most pronounced in the fourth quarter, when concentrations in the outflow peaked at 5 ng THg/L and 1.8 ng MeHg/L. At that time, MeHg was more than 16 times more concentrated in the outflow than the inflow. Mosquitofish, sunfish, and bass all exhibited a positive percent change across the STA, i.e., they contained higher levels in the discharge canal than in the supply canal. Levels of mercury in STA-2 mosquitofish were elevated compared to the other STAs and to several downstream sites. STA-2 bass also contained elevated levels of mercury compared to fish at the other STAs and at all but two downstream sites. Most importantly, the average THg concentration in bass collected in the discharge collection canal, when standardized to age class 3 years following the method of the Florida Fish and Wildlife Conservation Commission, was more than twice Florida's 0.5 parts per million (ppm) threshold for a limited fish consumption advisory to protect human health. By contrast, STA-2 sunfish were only slightly elevated in tissue-mercury when compared to fish at other STAs. Furthermore, STA-2 sunfish contained less mercury than fish from many downstream sites. Based on USEPA or FWS criteria, fish-eating wildlife appeared to be at some risk of adverse chronic effects from mercury exposure, especially if feeding preferentially on mosquitofish or small bass. Appendix 2B-7 discusses the results of the special mercury studies initiated to more accurately characterize the anomalous mercury behavior of STA-2.

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## INTRODUCTION

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This is the annual permit compliance monitoring report for mercury in STAs. This report summarizes the mercury-related reporting requirements of the Florida Department of Environmental Protection (FDEP) Everglades Forever Act permits (Ch. 373.4592, Florida Statutes [F.S.]), including permits for STA-6, STA-5, STA-1W, and STA-2 (No. 06,502590709, 262918309, 0131842, FL0177962-001, 0126704). This report summarizes the results of monitoring in Water Year 2003 (May 1, 2002 through April 30, 2003). The results of mercury monitoring at sites downstream of the STAs (non-Everglades Construction Project [non-ECP] discharge structures and marshes) are reported separately in Appendix 2B-3 of this report.

This report consists of summarized key findings and an overall assessment, an introduction and background, a summary of the Mercury Monitoring and Reporting Program, and monitoring results. The background section briefly summarizes the operation of the STAs and discusses their possible impact on South Florida's mercury problem. The section also includes site descriptions and maps of each STA currently being monitored (in the order in which they became operational). The following section summarizes sampling and reporting requirements of the Mercury Monitoring Program within the STAs. Monitoring results are summarized and discussed in two subsections: (1) results from pre-operational monitoring, and (2) results from STA operational monitoring. Recent results from the Mercury Monitoring and Reporting Program describe significant spatial distributions and, in some instances, between-year differences in mercury concentrations.

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## BACKGROUND

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The STAs are treatment marshes designed to remove phosphorus from stormwater runoff originating from upstream agricultural areas and Lake Okeechobee releases. The STAs are being built as part of the Everglades Construction Project (ECP). When completed, the ECP will include seven STAs totaling about 50,000 acres of constructed wetlands. The downstream receiving waters to be restored and protected by the ECP include the South Florida Water Management District's (SFWMD or District) water management canals of the Central and Southern Florida (C&SF) Project and the interior marshes of the Everglades Protection Area (EPA), encompassing Water Conservation Areas 1, 2A, 2B, 3A, and 3B, the Arthur R. Marshall Loxahatchee National Wildlife Refuge, and the Everglades National Park (ENP or Park).

Atmospheric loading is often the dominant, proximate source of inorganic mercury to many water bodies, with the ultimate primary drivers being coal-fired utility boilers and municipal and medical waste incinerators. However, understanding the ultimate cause of the mercury problem in the Everglades and some STAs is complicated by the fact that the mercury problem is a methylmercury (MeHg) problem, not an inorganic mercury or elemental mercury problem. Methylmercury is produced from inorganic mercury in rain, runoff, and sediments or flooded soils by primarily sulfate-reducing bacteria present in aquatic ecosystems. MeHg is highly toxic and magnifies up the food chain (biomagnifies) to levels that have impaired the Everglades sport fishery and that could threaten some sensitive, highly exposed members of some fish-eating wildlife species, including endangered species such as the wood stork and Everglades mink. Florida does not have a separate WQS for MeHg, but USEPA has published a water quality criterion of 0.3 parts per million (ppm) (also expressed as mg/kg) THg as MeHg in fish flesh to protect human health. The problem is further complicated by the fact that sulfate-reducing bacteria are stimulated by environmental sulfate up to a point, but the buildup of sulfide, the product of sulfate metabolism by these bacteria, can inhibit methylation beyond a certain point. This results in a parabolic relationship between sulfate concentration and MeHg production rather than the more traditional self-limiting logistics relationships, such as those observed in enzyme kinetics studies, for example. Unfortunately, where these breakpoints occur cannot yet be predicted from water or soil chemistry and biogeochemical first-principles.

Widespread, elevated concentrations of mercury were first discovered in freshwater fish from the Florida Everglades in 1989 (Ware et al., 1990). Subsequently, elevated concentrations of mercury were also found in predators, such as raccoons, alligators, Florida panthers, and wading birds (see Fink et al., 1999). To provide assurance that the ECP is not exacerbating the mercury problem, the SFWMD monitors concentrations of THg and MeHg in various abiotic (e.g., water and sediment) and biotic (e.g., fish and bird tissues) media.

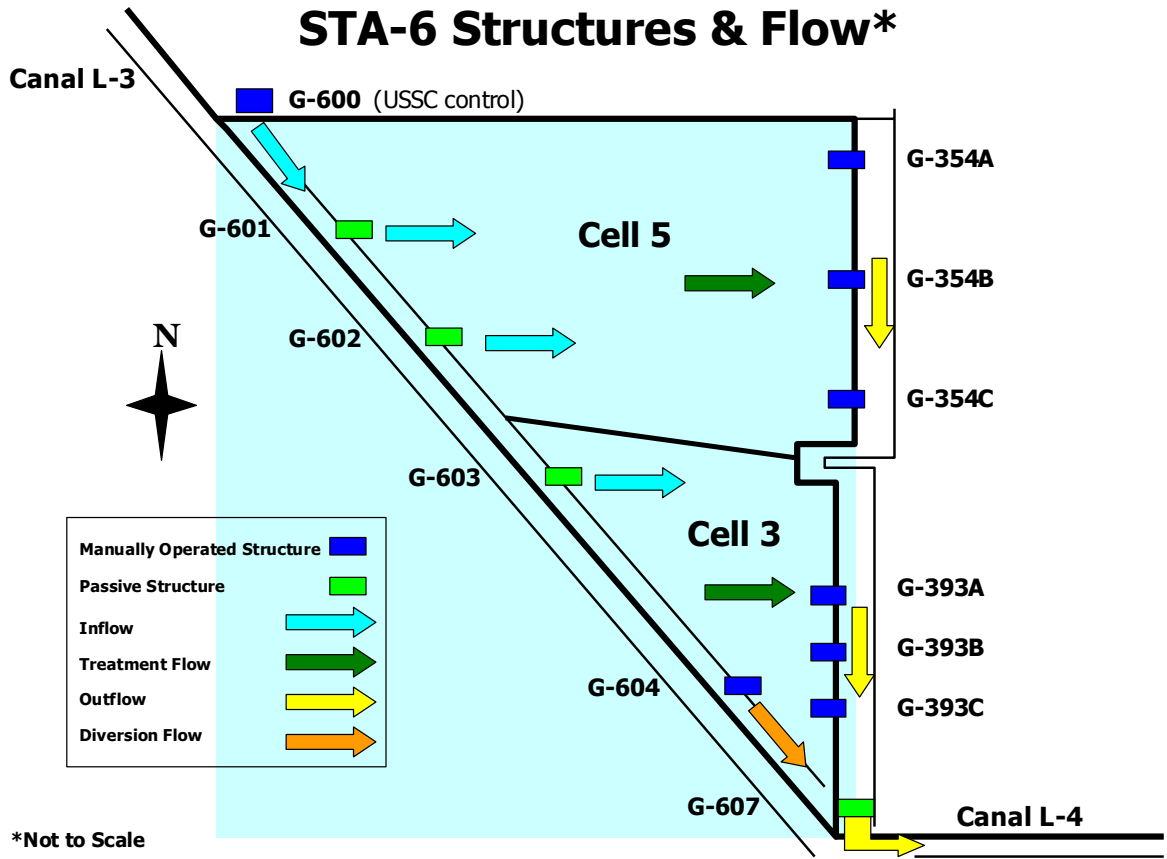
## SITE DESCRIPTIONS

### STA-6

STA-6, section 1 is located at the southeastern corner of Hendry County and the southwest corner of the Everglades Agricultural Area (EAA). STA-6, section 1 has two treatment cells (Cell 5, with an area of 252 ha, and Cell 3, with an area of 99 ha) that are designed to provide a total effective treatment area of 352 ha (870 acres) (**Figure 1**). (For additional details, see SFWMD, 1997.) The U.S. Sugar Corporation has operated the two cells as a stormwater retention area since 1989. Approximately 4,210 ha of U.S. Sugar's agricultural production area (Southern Division Ranch, Unit 2) drains into STA-6, section 1 via a supply canal and an existing pump station, G-600, that continues to be under U.S. Sugar's operation. Water flows from the supply canal to the treatment cells via supply canal weirs (two for Cell 5 and one for Cell 3). Water then flows in an easterly direction and is discharged through six recently installed culverts (G-354A, B, and C for Cell 5; G-393A, B, and C for Cell 3), each with a fixed-crest weir at 13.6 ft NGVD (National Geodetic Vertical Datum) to limit drawdown of each treatment cell to the desired static water level of 13.6 ft NGVD (for a maximum combined discharge of 500 cubic feet per second [cfs]). This outfall then enters the discharge canal, which gravity discharges to the L-4 borrow canal via six culverts, which are confluent to G-607. The L-4 borrow canal conveys flows eastward to the S-8 pump station, which discharges into Water Conservation Area 3A (WCA-3A). On demand, water can be conveyed from the L-4 canal backward (using stop logs at G-604 to bypass flows to the L-4 canal from the G-607 culverts) to the U.S. Sugar Corporation's Unit 2 farm for irrigation. As a consequence (unlike in other STAs), timing, quantity, duration of inflows and backflows, and, thus, mean depth, hydraulic loading rate, and hydraulic residence time (HRT) of STA-6 are controlled by U.S. Sugar Corporation via the operation of G-600.

### STA-5

STA-5 is immediately north of U.S. Sugar Corporation's Southern Division Ranch, Unit 2. It extends from the L-3 levee on the west to the Rotenberger Wildlife Management Area on the east. STA-5 consists of two parallel treatment cells (Cell 1 and Cell 2) to provide a total effective treatment area of 1,666 ha (4,118 acres) (**Figure 2**). (For additional details, see SFWMD, 1998a.) Under typical operations, water from three canals (L-3 borrow, Deer Fence, and S&M) gravity-flow into the two treatment cells through four gated supply canal culverts (G-342A, G-342B, G-342C, and G-342D). Water then continues to gravity-flow east through the western portions of the treatment area through eight open culverts into the eastern treatment areas. Each treatment cell is subdivided by an internal levee because of a significant downward slope in ground elevation from west to east. Water then gravity-flows through four discharge structures (G-344A and G-344B for Cell 1, and G-344C and G-344D for Cell 2) and then discharges into the STA-5 discharge canal. The STA-5 discharge canal continues along the western and northern sides of the Rotenberger Wildlife Management Area, ultimately emptying into the Miami Canal. However, direct discharge to the Rotenberger Tract is possible. This is used to supplement the natural accumulation of water via rainwater on an as-needed basis.



**Figure 1.** Map of STA-6.

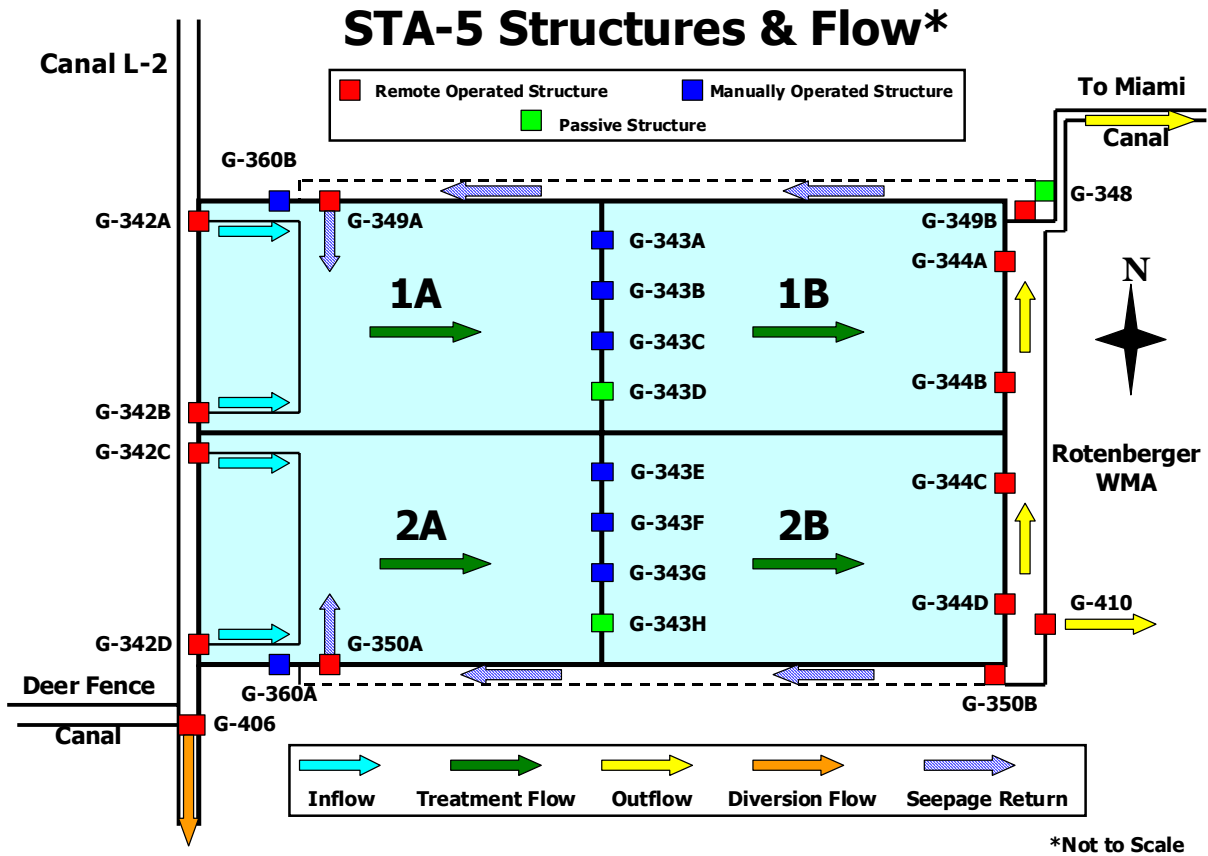


Figure 2. Map of STA-5.

## STA-1 West

STA-1 West is located in western Palm Beach County, northwest of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge). STA-1W is designed to provide a total effective treatment area of 6,870 acres, including the 3,815 acres of the existing Everglades Nutrient Removal (ENR) Project (Cells 1 through Cell 4), which it subsumed in April 1999 (**Figure 3**) (For additional details, see SFWMD, 1998b.) Under typical operations, S-5A basin runoff is conveyed to STA-1W from pump station S-5A via the STA supply canal and distribution works gated weir structure G-302. Flows will travel in a southwesterly direction via the supply canal into Cell 5 via culverts G-304A through G-304J, and into Cells 1 through 4 (the existing ENR Project) via gated weir structure G-303. Flows through Cell 5 are conveyed in a westerly direction through structures G-305A through G-305V and are discharged through culverts G-306A through G-306J and into the discharge canal. This discharge is then conveyed to WCA-1 via this canal and via pump station G-310. Flows through Cells 1 through 4 are conveyed in a southerly direction through G-252 and G-253 (for Cells 1 and 3) and G-254, G-255, and G-256 (for Cells 2 and 4). Flows are discharged into WCA-1 via existing ENR Project collection canals, existing pump station G-251, and, under some conditions (when ENR Project outflows exceed the G-251 pump capacity of 450 cfs), through structures G-258, G-259, G-308, and G-309 into discharge canal and pump station G-310. Thus, there are two primary discharge locations for STA-1W into the L-7 canal located in the Refuge.

## STA-2

STA-2 is located in western Palm Beach County near the Browns Farm Wildlife Management Area. STA-2 was developed to provide a total effective treatment area of 6,430 acres. Cell 1 is 1,990 acres; Cells 2 and 3 are 2,220 acres each. (For additional details, see SFWMD, 1999a.) STA-2 is intended to treat discharges from the S-6/S-2 basin, the S-5A basin, the East Shore Water Control District, 715 farms, and Lake Okeechobee via pump stations S-6 and G-328. S-6 will serve as the primary supply canal pumping station, with G-328 serving as both irrigation and “secondary” supply canal source from and to the STA supply canal (**Figure 4**). G-328 serves approximately 9,980 acres of adjacent agricultural lands. Discharges from the supply canal are then conveyed southward to the supply canal, which extends across the northern perimeter. A series of supply canal culverts will then convey flows from the supply canal to the respective treatment cells (G-329A through G-329D into Cell 1; G-331A through G-331G into Cell 2; G-333A through G-333E into Cell 3). Flows will travel southward through the treatment cells, eventually discharging to the discharge canal via culverts or gated spillways (culverts G-330A through G-330E from Cell 1; gated spillway G-332 from Cell 2; gated spillway G-334 from Cell 3). Flows then travel eastward in the discharge canal to the STA-2 outflow pump station, G-335, which in turn conveys water to a short stub canal leading to the L-6 borrow canal. Water in the L-6 borrow canal will travel north and then east into WCA-2A through six box culverts (each with a capacity of 300 cfs, invert at 12 ft), located east of G-339 about three miles south of S-6. The area to receive discharge was previously identified as a nutrient-impacted area. Under high-flow conditions, when stage in the L-6 canal exceeds 14.25 ft, water in the L-6 borrow canal will spill into five 72-inch cans and travel south toward S-7. Approximately 0.75 miles north of S-7, the berm has been degraded to an elevation of approximately 12 ft, allowing water to sheetflow into WCA-2A. Here again, the area to receive discharge was previously identified as a nutrient-impacted area.

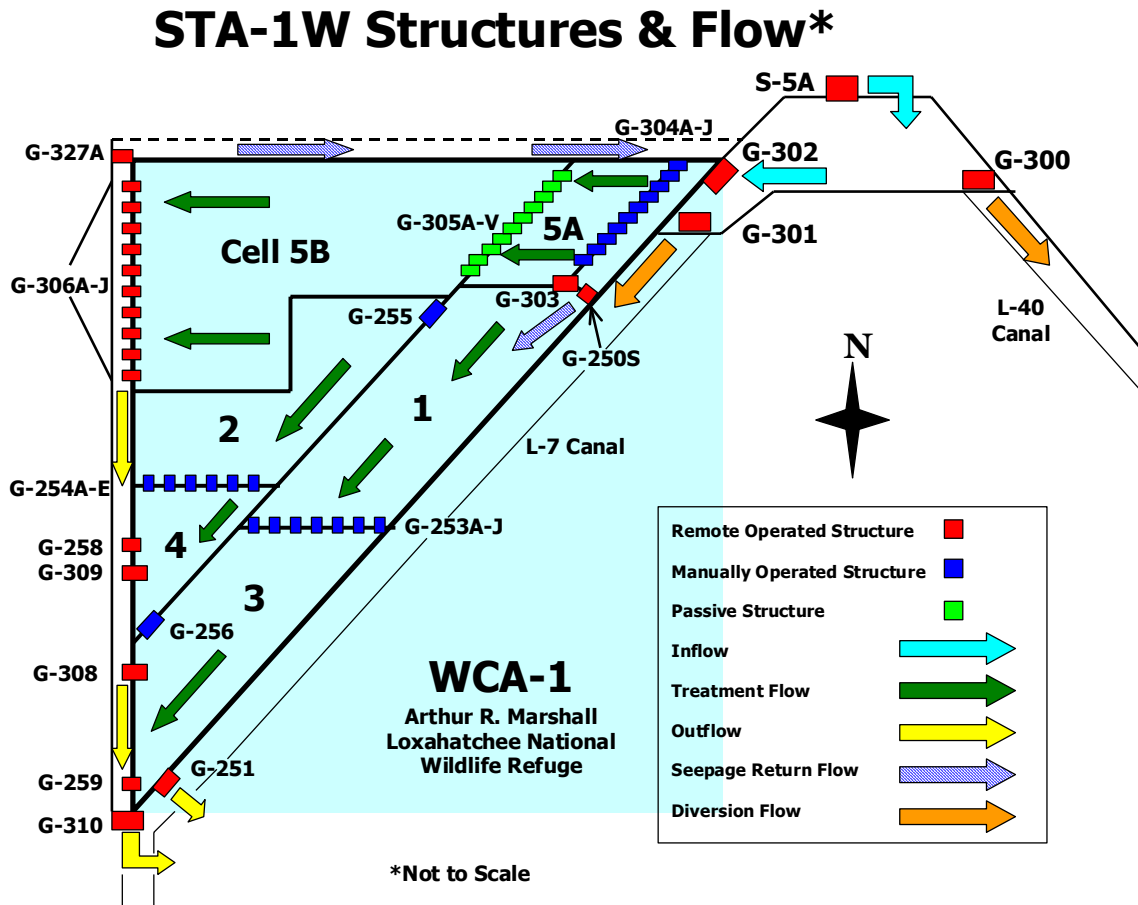


Figure 3. Map of STA-1W.



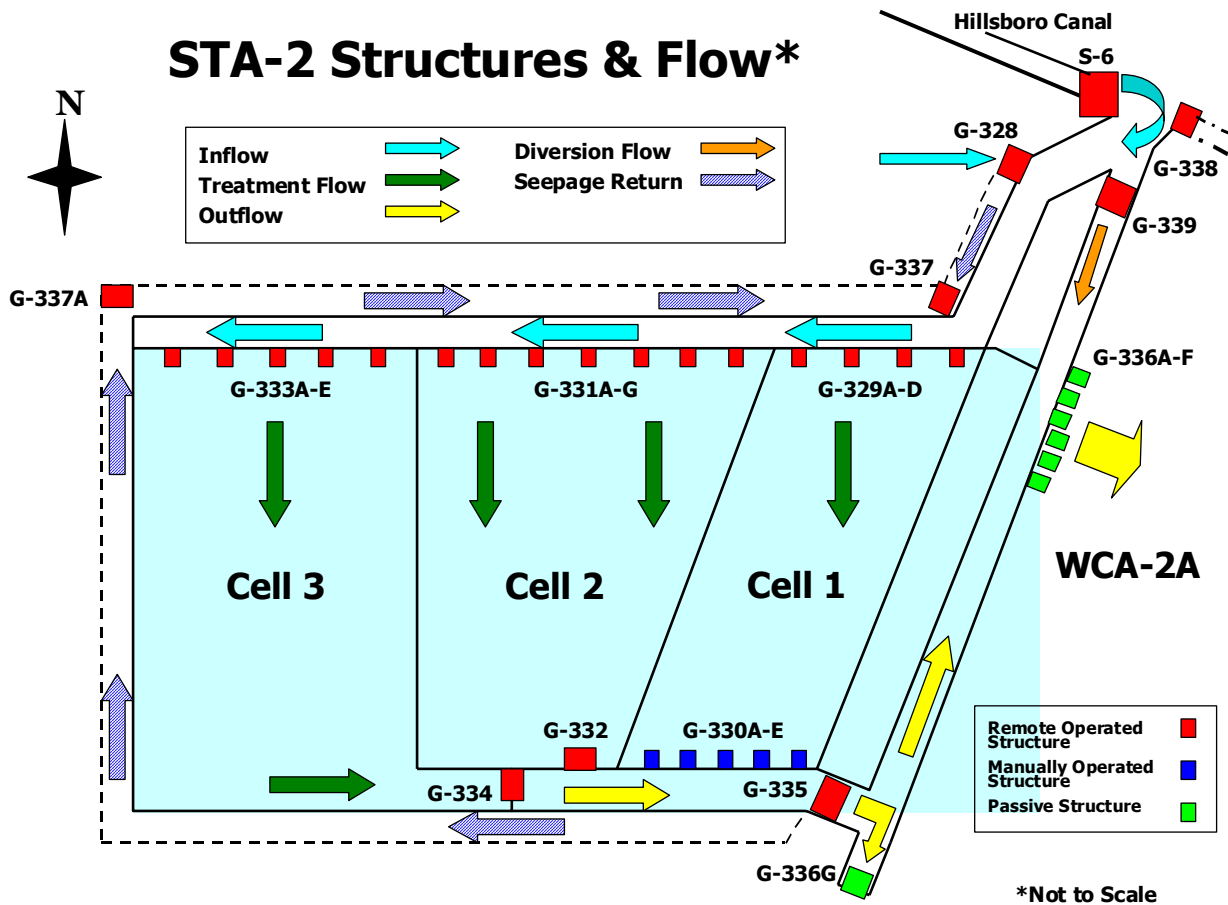


Figure 4. Map of STA-2.

## SUMMARY OF THE MERCURY MONITORING AND REPORTING PROGRAM

The monitoring and reporting program summarized below is described in detail in the Mercury Monitoring and Reporting Plan for the Everglades Construction Project, the Central and Southern Florida Project, and the Everglades Protection Area. This was submitted by the SFWMD to the Florida Department of Environmental Protection (FDEP), the U.S. Environmental Protection Agency (USEPA), and the U.S. Army Corps of Engineers (USACE) in compliance with the requirements of the aforementioned permits. The details of the procedures to be used in ensuring the quality of and accountability for the data generated in this monitoring program are set forth in the SFWMD's Quality Assurance Project Plan (QAPP) for the Mercury Monitoring and Reporting Program, which was approved on issuance of the permit by the FDEP. QAPP revisions were approved by the FDEP on June 7, 1999.

## **EVERGLADES MERCURY BASELINE MONITORING AND REPORTING REQUIREMENTS**

Levels of THg and MeHg in the pre-operational soils of each of the STAs and various compartments (media) of the downstream receiving waters define the baseline condition from which to evaluate mercury-related changes, if any, brought about by the operation of the STAs. The pre-ECP mercury baseline conditions are defined in the Everglades Mercury Background Report, which summarized all of the relevant mercury studies conducted in the Everglades through July 1997. This was during the construction, but prior to the operation of, the first STA. Originally prepared for submittal in February 1998, the report was revised to include the most recent data released by the USEPA and the U.S. Geological Survey (USGS) and was submitted in February 1999 (FTN Associates, 1999).

### **PRE-OPERATIONAL MONITORING AND REPORTING REQUIREMENTS**

Prior to completion of construction and flooding of the soils of each STA, the District is required to collect 10-cm core samples of soil at six representative interior sites and to analyze them for THg and MeHg. Prior to initiation of discharge, the District is also required to collect biweekly samples of unfiltered water from each supply canal and a representative interior site from each independently operable treatment train for ultra-trace analysis for THg and MeHg concentrations. When concentrations at the interior sites are found not to be significantly greater than that of the supply canal (for STA-2 this demonstration was made using data for the period of record and a t-test at the 95-percent confidence level), this information is reported to the permit-issuing authority, and the biweekly sampling can be discontinued. Discharge begins after all the startup criteria are met.

This is followed by a stabilization period for both phosphorus and mercury. During this stabilization period, the release of stored phosphorus and mercury from flooded farm field soils is anticipated, with concomitant instances of outflow or interior concentrations exceeding supply canal concentrations. As the bioavailable phosphorus and mercury are transported from the soil reservoir to the colonizing plants and accreting marsh soils, the magnitude, duration, and frequency of such phenomena will decrease until stabilization is achieved and the outflow and interior concentrations are routinely less than the supply canal on an annual basis. The stabilization period ends when the 12-month moving, flow-weighted average total phosphorous (TP) concentration in the outflow is less than 50 ppb. Most of the STAs complete this stabilization period within two years of initiation of flow-through operation.

### **OPERATIONAL MONITORING**

Following approval for initiation of routine operation of an STA and thereafter, the permits require that the following samples be collected at the specified frequencies and analyzed for specified analytes:

**Water:** On a quarterly basis, 500-ml unfiltered grab samples of water are collected in pre-cleaned bottles using ultraclean technique at the supply canals and outflows of each STA. They are analyzed for MeHg and THg (this includes the sum of all mercury species in sample, e.g., Hg<sup>0</sup>, Hg<sup>I</sup>, and Hg<sup>II</sup>, as well as organic mercury). THg results are compared with the Florida Class III water quality standard of 12 ng/L to ensure compliance. Outflow concentrations of both THg and MeHg are compared to concentrations at the supply canal.

**Sediment:** Triennially, sediment cores are collected from 0-to-10 cm depth at six representative interior sites. Each depth-homogenized core is then analyzed for THg and MeHg.

**Prey fish:** Semiannually, grab samples of between 100 and 250 mosquitofish (*Gambusia* sp.) are collected using a dip net at the supply canal sites, interior sites, and outflow sites of each STA. Individuals are composited from each size, and the homogenate is subsampled in quintuplicate. Each subsample is then analyzed for THg. On March 5, 2002 the FDEP approved a reduction in the number of replicate analyses of the homogenate from five to three (correspondence from F. Nearhoof, FDEP).

**Top predator fish:** Annually, 20 largemouth bass are collected primarily via electroshocking methods at representative supply canal and discharge canal sites and representative interior sites in each STA. The fish muscle (fillet) samples are analyzed for THg as an indicator of potential human exposure to mercury.

In 2000, the District began routine collection of sunfish at the same frequency, intensity (i.e.,  $n = 20$ ), and locations as largemouth bass. This permit revision fulfilled a USFWS recommendation (USFWS recommendation 9b in USACE Permit No. 199404532.) (For details, see correspondence to Bob Barron, USACE, dated July 13, 2000). Sunfish, analyzed as whole fish, also serve as a surrogate for attempts to monitor mercury in wading birds that do not nest in the STAs. (For details on the monitoring program tracking mercury in wading birds in downstream areas, see Appendix 2B-3 of this report.) The addition of sunfish to the compliance monitoring program was approved by the FDEP on March 5, 2002 (correspondence from F. Nearhoof, FDEP).

It is important to note that virtually all (> 85 percent) of the mercury in fish tissues is in the methylated form (Grieb et al., 1990; Bloom, 1992; SFWMD, unpublished data). Therefore, the analysis of fish tissue for THg, which is a more straightforward and less-costly procedure than for MeHg, can be interpreted as being equivalent to the analysis of MeHg. Further details regarding rationales for sampling scheme, procedures, and data reporting requirements are set forth in the Everglades Mercury Monitoring Plan revised in March 1999 (Appendix 1 of QAPP, June 7, 1999).

## QUALITY ASSURANCE MEASURES

For a quality assurance/quality control assessment of the District's Mercury Monitoring Program during Water Year 2003, see Appendix 2B-3 of this report.

## STATISTICAL METHODS

As stated earlier, monitoring THg concentrations in aquatic animals provides several advantages. However, the proper interpretation of residue levels in animals can sometimes prove problematic due to the confounding influences of age or species of collected animals or of changes in range associated with changes in environmental conditions (e.g., marsh hydroperiod). For comparison, special procedures are used to normalize the data. Standardization is a common practice (Wren and MacCrimmon, 1986; Hakanson, 1980). To be consistent with the reporting protocol used by the FWC (Lange et al., 1998 and 1999), mercury concentrations in largemouth bass were standardized to an expected mean concentration of mercury in three-year-old fish (represented as EHg3) at a given site by regressing mercury against age (see Lange et al., 1999). To adjust for the month of collection, otolith ages were first converted to decimal ages using

protocols developed by Lange et al., 1999. Sunfish were not aged, so age normalization was not available. Instead, arithmetic means were reported. However, efforts were made to estimate a least square mean (LSM) Hg concentration based on the weight of the fish. Additionally, the distribution of the different species of *Lepomis* (warmouth, *L. gulosus*; spotted sunfish, *L. punctatus*; bluegill, *L. macrochirus*; and red ear sunfish, *L. microlophus*) that were collected during electroshocking was also considered as a potential confounding influence on Hg concentrations prior to each comparison.

Where appropriate, analysis of covariance (ANCOVA), using the SAS GLM procedure, was used to evaluate spatial and temporal differences in mercury concentrations, with age (largemouth bass) or weight (sunfish) as a covariate. However, use of ANCOVA is predicated on several critical assumptions (for review, see ZAR, 1996), including:

1. That regressions are simple linear functions
2. That regressions are statistically significant (i.e., nonzero slopes)
3. That the covariate is a random, fixed variable
4. That both the dependent variable and residuals are independent and normally distributed
5. That slopes of regressions are homogeneous (parallel)

Regressions also require that collected samples exhibit a relatively wide range of covariate, that is, that fish from a given site are not all the same age or weight. Where these assumptions were not met, ANCOVA was inappropriate. Instead, standard analysis of variance (ANOVA) or Student's t-tests (SigmaStat, Jandel Corporation, San Rafael, CA) were used. Possible covariates were considered separately and often qualitatively. The assumptions of normality and equal variance were tested by the Kolmogorov-Smirnov and Levene Median tests, respectively. Datasets that either lacked homogeneity of variance or departed from normal distribution were natural-log transformed and reanalyzed. If transformed data met the assumptions, they were used in ANOVA. If they did not meet the assumptions, then raw data sets were evaluated using nonparametric tests, such as the Kruskal-Wallis ANOVA on ranks or the Mann-Whitney Rank sum test. If the multigroup null hypothesis was rejected, groups were compared using either Tukey HSD (honestly significant difference) or Dunn's method.

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## MONITORING RESULTS

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### PRE-OPERATIONAL MONITORING

#### STA-6, Section 1

As previously reported (SFWMD, 1998c), STA-6, section 1 met startup criteria for mercury in November 1997, and it began operation in December 1997.

#### STA-5

As reported in the *2003 Everglades Consolidated Report* (Rumbold et al., 2001a), STA-5 met startup criteria for mercury in September 1999.

## STA-1W

As reported in the *2003 Everglades Consolidated Report* (Rumbold et al., 2001a), the permit for STA-1W was issued on May 11, 1999. STA-1W passed startup criteria during the week of January 17, 2000; flow-through operations began in early February 2000.

## STA-2

STA-2 Cell 3 and Cell 2 met mercury startup criteria on September 26, 2000 and November 9, 2000, respectively. Cell 1 did not meet startup criteria until November 26, 2002. (For previous results of startup and expanded mercury monitoring, see Rumbold and Fink, 2003. For results of expanded studies during Water Year 2003, see Appendix 4A-7 of this report).

## OPERATIONAL MONITORING

### STA-6

Routine monitoring of mercury at STA-6 began in the first calendar quarter of 1998. Results of monitoring prior to April 30, 2002 have been reported previously (SFWMD, 1998c and 1999c; Rumbold and Rawlik, 2000; Rumbold et al., 2001a; Rumbold and Fink, 2002; Rumbold and Fink, 2003).

As is evident from data shown in **Table 1** and **Table 2**, which are graphically presented in **Figure 5**, concentrations of THg and MeHg spiked in STA-6 outflows during the second quarter of 2002. On the day of the sample collection (June 20, 2002), the concentration of THg and MeHg reached 8.8 ng/L and 6.5 ng/L, respectively, just upstream of the outflow culvert of Cell 5. This was similar to the spike that occurred one year earlier (**Figure 5**), except that the magnitude of the MeHg spike was two times higher and, this time, concentrations were greater in the outflow of Cell 5 as compared to Cell 3. As discussed in earlier reports (Rumbold et al., 2001b), previous concentrations of both THg and MeHg in sediment, surface water, and fish were typically greater in Cell 3. As discussed in the *2003 Everglades Consolidated Report* (Rumbold and Fink, 2003), proper interpretation of these concentration spikes must consider seasonal rainfall and other hydrologic factors that can affect loading of inorganic mercury and net MeHg production.

From mid-April through mid-June 2002, STA-6 had experienced a drydown in both Cell 3 and Cell 5. (Cell 5 dried out one week earlier than Cell 3.) The STA was then reflooded after receiving over 10 inches of rain in the three weeks prior to the June sample collection. This sequence of events (drydown and reflooding with direct rainfall) was similar to those preceding the 2001 spikes and likely contributed to the observed spike in both THg and MeHg in 2002.

Rain in South Florida typically contains approximately 12 ng THg/L. This is the median of period of record for three South Florida stations in the National Atmospheric Deposition Program's (NADP) Mercury Deposition Network (MDN) (see Appendix 2B-3). However, THg levels in South Florida's rain can exceed 62 ng/L. Once deposited, this mercury, which is primarily inorganic, is rapidly processed and assimilated as it enters the marsh (e.g., oxidation, sorption, deposition, methylation), or it quickly evades back to the atmosphere. Thus, THg concentration is typically greater in rainfall than in surface water. Obviously, recently deposited Hg in rainfall can dramatically increase surface water concentrations of THg. Furthermore, this atmospherically deposited Hg has been found to be highly bioavailable to sulfate-reducing

**Table 1.** Concentrations of total mercury (THg) and methylmercury (MeHg) in surface waters collected quarterly from the STAs (units ng/L).

STA	THg (ng/L)					MeHg (ng/L)				%MeHg		
	Quart	Inflow	Remark*	Outflow	remark	THg WQS†	Inflow	remark	Outflow	remark	Inflow	Outflow
STA 6	02-2	2.80		7.70		<WQS	0.690		4.650		25%	60%
	02-3	NA	V	NA	V	<WQS	0.220		0.247		NA	NA
	02-4	1.30		0.42		<WQS	0.150		0.044		12%	11%
	03-1	1.50		0.84		<WQS	0.520		0.085		35%	10%
STA 5‡	02-2	2.78		3.77		<WQS	0.485		0.120		17%	3%
	02-3	5.18		8.15		<WQS	0.223		0.275		4%	3%
	02-4	1.53		0.51		<WQS	0.150		0.090		10%	18%
	03-1	1.33		1.08		<WQS	0.195		0.393		15%	36%
STA 1W§	02-2	1.50	J5	0.88	J5	<WQS	0.057		0.065		4%	7%
	02-3	4.50		1.15		<WQS	0.074		0.097		2%	8%
	02-4	5.30		1.03		<WQS	0.160		0.058		3%	6%
	03-1	1.20		0.46		<WQS	0.300		0.068		25%	15%
STA 2**	02-2	0.76		1.10		<WQS	0.100		0.250		13%	25%
	02-3	1.35		1.80		<WQS	0.300		0.360		22%	23%
	02-4	0.68		5.00		<WQS	0.108		1.800		16%	36%
	03-1	1.75		2.00		<WQS	0.180		0.810		10%	41%

\* For qualifier definitions, see FDEP rule 62-160: "A" - averaged value; "U" - undetected, value is the MDL; "I" - below PQL; "J" - estimated value, the reported value failed to meet established QC criteria;

"J3" -estimated value, poor precision, "V" - analyte detected in both the sample and the associated method blank.

† Class III water quality standard of 12 ng THg / L.

‡ "NC" – not calculated; "NO" – no outflow at the time of sampling.

‡ STA 5 has multiple inflows and outflows and reported value represents mean of valid data (unqualified).

§ STA 1W has a single inflow and two outflows; the reported value for the latter represents mean of valid data (unqualified).

\*\* STA 2 has two inflow monitoring points (G-328 and S6) and a single outflow; the reported value for the latter represents mean of valid data (unqualified).

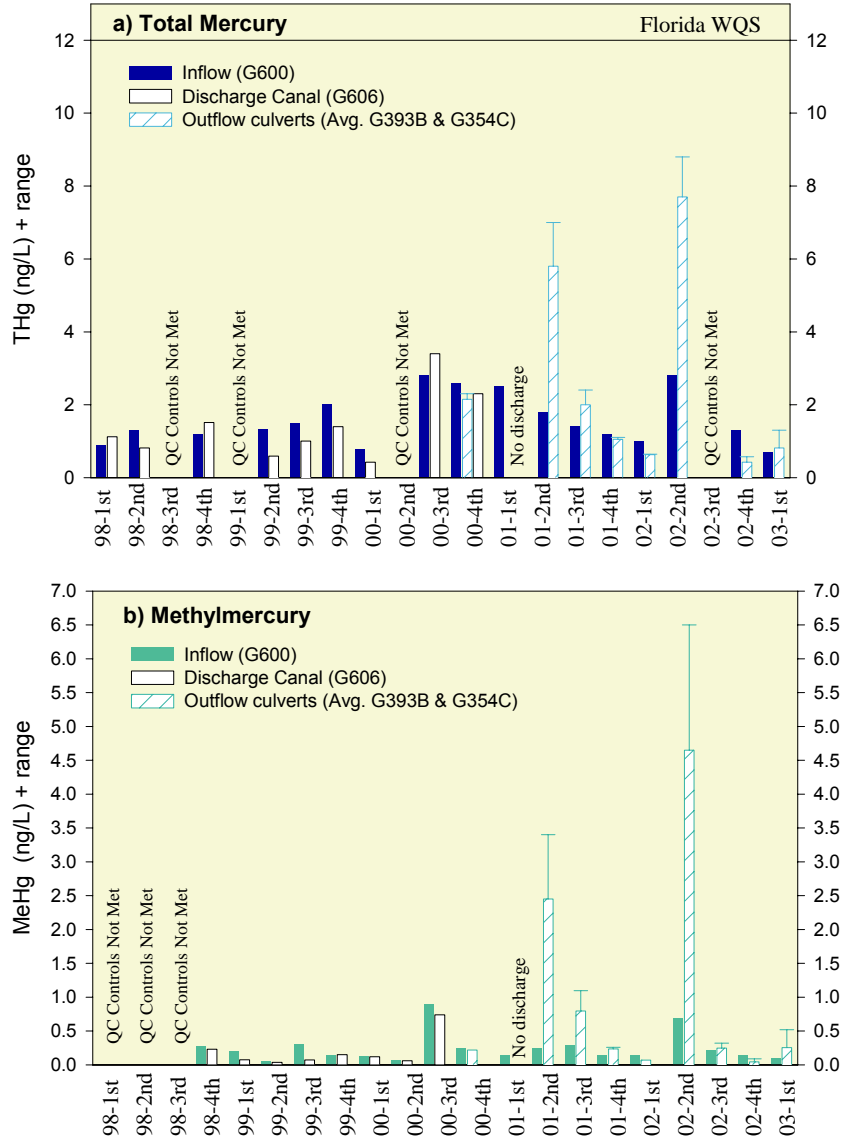
**Table 2.** Percent change in concentration of THg and MeHg in surface water across STAs (i.e., outflow-inflow/inflow)

STA	Quarter	THg	MeHg
STA 6	Jun-02	175%	574%
	Sep-02	NA	12%
	Dec-02	-68%	-70%
	Mar-03	-44%	-84%
Annual average		21%	108%
Cumulative average		9%	75%
STA 5	02-2	36%	-75%
	02-3	57%	24%
	02-4	-67%	-40%
	03-1	-18%	101%
Annual average		2%	2%
Cumulative average		3%	9%
STA 1	02-2	-41%	14%
	02-3	-74%	30%
	02-4	-81%	-64%
	03-1	-62%	-78%
Annual average		-65%	-24%
Cumulative average		-45%	-13%
STA 2	02-2	46%	150%
	02-3	33%	20%
	02-4	641%	1567%
	03-1	14%	350%
Annual average		184%	522%
Cumulative average		160%	449%

\*\* Only valid (unqualified) data used in calculations; see Table 1 for raw data and qualifiers.

bacteria that mediate methylation (D. Krabbenhoft, USGS, personal communication). A sequence of drydown and oxidation of sediments, followed by summer rains, has been found to have a profound effect on mercury biogeochemistry, which can lead to stimulated MeHg production (Krabbenhoft and Fink, 2001). It is noteworthy that the concentrations of both THg and MeHg declined to more typical levels by the following month (i.e., average outflow concentrations were 2.6 ng THg/L and 0.41 ng MeHg/L) (**Table 1**). At no time during the reporting year did THg concentration exceed the Class III water quality standard of 12 ng/L. More importantly, as discussed below, this spike in surface water MeHg concentration was not reflected in tissue concentrations of mercury in the STA-6 fishes that respond rapidly to such MeHg anomalies (i.e., mosquitofish) or in those fish that integrate MeHg exposure over a much longer period (i.e., sunfish and largemouth bass).

### STA-6 Surface Water



**Figure 5.** Concentration of (a) total mercury (THg) and (b) methylmercury (MeHg) in unfiltered surface water collected at STA-6.

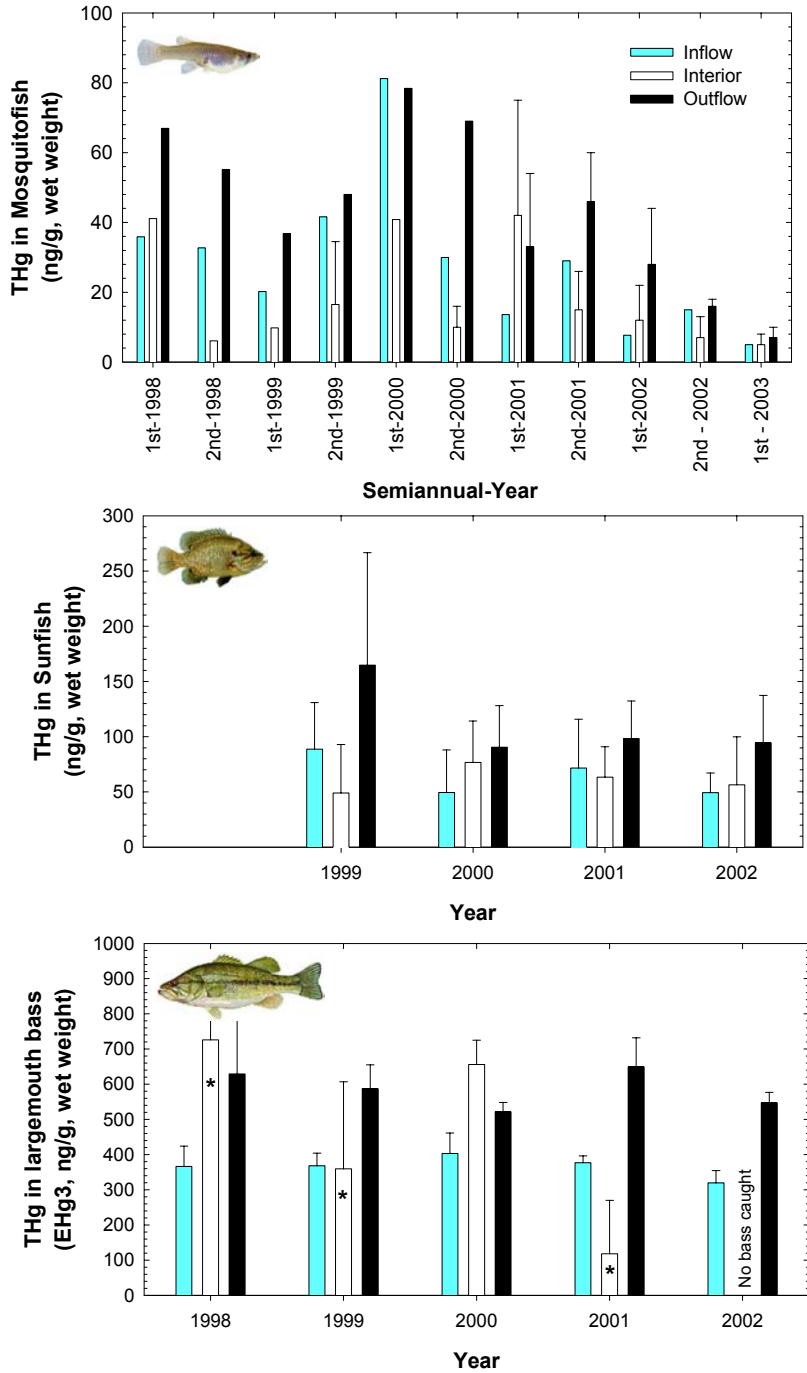


To more fully understand the conditions that preceded the spike in water column MeHg, monitoring was expanded in July 2002 to include monthly sampling of water, sampling at a second outflow culvert from Cell 5 (G-354A) and a one-time sediment collection. Results of this expanded monitoring program are reported in Appendix 2B-6.

Levels of mercury in mosquitofish from STA-6 were relatively low during the second half of 2002 and the first half of 2003, approaching levels observed at the ENR Project (**Figure 6** and **Figure 10**). This is particularly noteworthy given the spike in MeHg that occurred in surface water during the second quarter of 2002. However, it should be noted that the semiannual collection of mosquitofish occurred three months after the MeHg spike in the water column. Because of this, it may not have captured the MeHg bioavailability immediately following the spike. Nevertheless, the mosquitofish do indicate that the spike in MeHg was short-lived, thus confirming the surface water grab collected a month after the spike. Moreover, as shown in **Table 3**, levels of THg were very similar between inflow and outflow composites, and the positive percent change in mosquitofish THg burdens across the STA for the year was much reduced compared to previous years. Further, as is evident from the range bars shown in **Figure 6**, mosquitofish from the two cells also are more similar in THg levels than in previous years (both in the interior and just upstream of outflow culverts).

Similar to the mosquitofish, visual inspection of the data presented in **Figure 6** shows no obvious change in body burdens of STA-6 sunfish following the MeHg spike in the water column. A corollary to this is that, unlike mosquitofish, STA-6 sunfish have not shown any consistent temporal trends in Hg (upward or downward) over the last four years. Although Hg levels varied in sunfish both from the interior (Cell 5 only) and the discharge canal (ANOVA on Ranks,  $H = 12.612$ ,  $df = 3$ ,  $P = 0.006$ ;  $H = 9.678$ ,  $df = 3$ ,  $P = 0.022$ , respectively), pairwise comparisons reveal only 1999 and 2000 fishes differed significantly (Dunn's post hoc test  $p < 0.05$ ). Interestingly, relative to 1999, Hg levels were higher in Cell 5 sunfish but lower in discharge sunfish in 2000. STA-6 sunfish demonstrated location-related differences in Hg concentration (ANOVA,  $df = 2$ , 50;  $F = 8.9$ ,  $P < 0.001$ ). Sunfish from the discharge canal contained greater Hg levels than both fish from the interior and supply canal (Tukey test,  $p < 0.05$ ). Although the sunfish also exhibited location-related differences in total length ( $df = 2$ , 50;  $F = 7.1$ ,  $P = 0.002$ ), fish in the discharge canal were smaller than supply fish. Thus, this would not likely account for higher levels (smaller fish in the discharge canal would more likely have lower levels, if other things were equal). Differences in species composition of sampled *Lepomis* sp. also did not appear to be sufficient to account for spatial patterns in Hg burdens in sunfish. Consequently, sunfish continued to exhibit a positive percent change in Hg across the STA (**Table 4**).

Results from operational monitoring of mercury concentrations in largemouth bass from STA-6 are summarized in **Table 5** and are graphically displayed in **Figure 6**. Similar to sunfish, largemouth bass collected over the last five years from the STA-6 discharge canal contained greater tissue mercury concentrations than fish from the supply canal, i.e., positive percent change (**Table 5** and **Figure 6**). Previously, this difference in Hg concentration has been shown to be significant by ANCOVA, which can partition the effects of differences in age. Because of an interaction between the effects of fish age and location on mercury concentration, ANCOVA could not be used to assess difference in Hg levels in bass collected in supply and discharge canals in 2002 (ANOVA,  $df = 1$ , 40;  $P = 0.036$ ).



**Figure 6.** Mercury concentrations in (top) mosquitofish composites (+ range), (middle) whole sunfish ( $\pm$  SD), and (bottom) fillets of largemouth bass ( $\pm$  95% CI or, if arithmetic, SD) collected at STA-6. Note: The latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (\* for details, see **Table 5**), in which case the arithmetic mean is reported.

**Table 3.** Concentration of total mercury (THg) in mosquitofish composites collected semi-annually from STAs (units ng/g wet weight)

STA	Half-year	Inflow fish	Interior fish	Outflow fish	Percent change
STA 6	2002-2	15	7 ±6	16 ±2	7%
	2003-1	5	5 ±3	7 ±3	40%
	Annual mean	10	6	11	10%
Cumulative mean		28 ±21	19 ±15	44 ±23	57%
STA 5	2002-2	15 ±2	5 ±2	9 ±0.5	-40%
	2003-1	16 ±1	11 ±2	17 ±4	6%
	Annual mean	15	8	13	-13%
Cumulative mean		34 ±11	31 ±31	32 ±18	-6%
STA 1W	2002-2	18	2 ±1	13 ±1	-28%
	2003-1	13	8 ±5	9 ±1	-31%
	Annual mean	15	5	11	-27%
Cumulative mean		36 ±47	13 ±7	23 ±27	-36%
STA 2	2002-2	4	38 ±38	167	-28%
	2003-1	4	44 ±40	64	-31%
	Annual mean	4	41	116	-27%
Cumulative mean		11 ±8	94 ±67	189 ±111	-36%

\* Mosquitofish are collected semi-annually at inflow, interior and outflow sites.

† - Standard deviation is reported where multiple composites are collected from location (e.g., multiple inflows or outflows, multiple cells); range is reported where two sites are sampled; other values represent mean of five analyses of a single composite sample.

Note: per FDEP approval (March 5, 2002), the number of aliquots was reduced from 5 to 3.

Note: per FDEP approval (March 5, 2002), collection locations were reduced from 4 to 2 for both the inflow and outflow of STA 5.

‡ - Percent change = outflow-inflow / inflow

**Table 4.** Concentration of total mercury (THg, ng/g wet weight) in sunfish (*Lepomis* spp.) collected from STAs in 2002 (sample size in parentheses)

STA	Inflow fish	Interior fish	Outflow fish	Percent Change <sup>a</sup>
STA 6	49 ±18 (20)	57 ±43 (11 <sup>b</sup> )	94 ±43(20)	92%
Cum. mean <sup>c</sup>	65	61	112	72%
STA 5	78 ±52(20)	58(1)	NA	NA
Cum. mean	81	100	112	38%
STA 1W	29 ±8 (20)	19 ±15 (60 <sup>b</sup> )	18 ±19 (37 <sup>b</sup> )	-38%
Cum. mean	39	24	26	-33%
STA 2	42 ±43 (20)	64 ±47 (60 <sup>b</sup> )	122 ±126 (20)	190%
Cum. mean	73	91	141	93%

a. Percent change = outflow-inflow / inflow

b. Where n > 20; multiple sites were sampled and pooled, i.e., multiple interior or outflows.

c. Grand mean of annual means; sunfish collected in 1999, prior to permit revision or STA operation (in the case of STAs 5 and 1W) were included in the cumulative average.

**Table 5.** Standardized, EHg3  $\pm$  95%, and arithmetic mean concentration (mean  $\pm$  1SD, n; in parentheses) of total mercury (ng/g, wet weight) in fillets from largemouth bass collected at STAs in 2002.

STA	Inflow fish	Interior fish	Outflow fish	Percent change <sup>‡</sup>	Consumption advisory exceeded
STA-6	319 $\pm$ 35 (263 $\pm$ 103, 20)	NA NA	547 $\pm$ 30 (540 $\pm$ 190, 20)	71%	Yes
Cumulative mean	287(b)	438(b)	548(b)	88%	
STA-5	NC (1) (117 $\pm$ 19, 13)	NA NA	NA NA	NA%	Unknown
Cumulative mean*	235(b)	403(b)	440(b)	87%	
STA-1W	226 $\pm$ 43 (241 $\pm$ 171, 19)	104 $\pm$ 14 (81 $\pm$ 83, 51†)	NC (1) (56 $\pm$ 30, 33†)	-77%	No
Cumulative mean*	270(b)	80(b)	79(b)	-71%	
STA-2	509 $\pm$ 184 (262 $\pm$ 273, 20)	402 $\pm$ 78 (319 $\pm$ 291, 49†)	1169 $\pm$ 233 (1089 $\pm$ 507, 20)	316%	Yes
Cumulative mean*	286(b)	322(b)	979(b)	252%	

\* Bass collected in 1999 prior to operation of STAs 5 and 1W were included in the cumulative average (a) based on EHg3, or (b) based on arithmetic mean.

† - Where n > 20; multiple sites were sampled and pooled, i.e., multiple interior or outflows.

‡ - Percent change = outflow-inflow / inflow.

¶ Florida limited consumption advisory threshold is 500 ng/g in three-year-old bass.

NC = not calculated, where: (1) regression slope was not significantly different from 0, or (2) poor age distribution of collected fish.

In terms of temporal trends, Hg levels in bass collected from the supply canal did not differ among years (ANCOVA,  $df = 4, 84$ ;  $F = 1.86$ ;  $P = 0.124$ ). Alternatively, levels have changed over time in bass from the discharge canal. As reported last year (Rumbold and Fink, 2003), from 1998 to 2000, Hg levels had declined in bass from the discharge canal but then increased in 2001. An ANCOVA of the five-year period of record demonstrated a significant difference among years ( $df = 4, 93$ ;  $F = 3.24$ ,  $P = 0.01$ ), but a Tukey post hoc test revealed only 2000 and 2001 differed ( $P = 0.04$ ). It is important to realize that tissue burdens in bass caught in 1998, less than one year after startup of the STA, probably reflected conditions prior to its operation as a Stormwater Treatment Area. Therefore, the lack of statistically significant difference with 1998 levels suggests conditions have not changed subsequent to SFWMD's assuming operation of the STA. Despite a good faith effort, no bass were caught in the interior marshes of STA-6 in 2002.

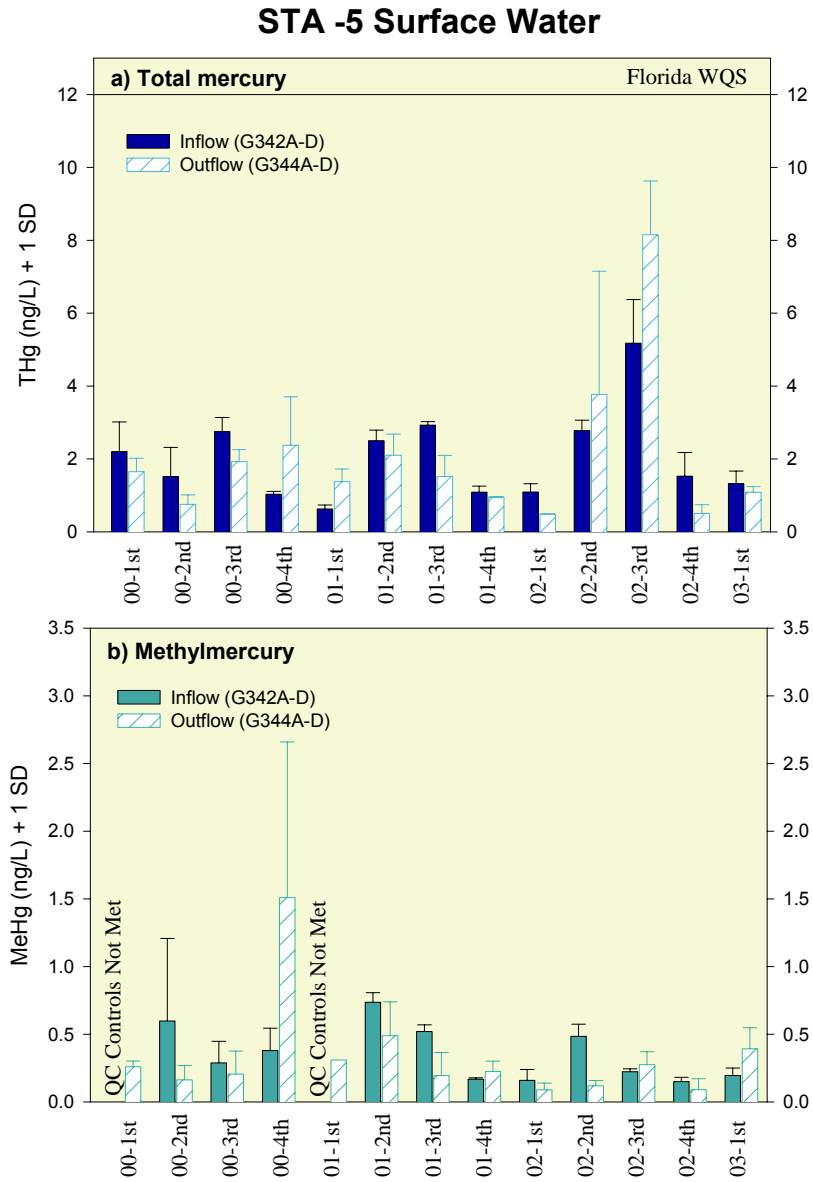
Levels of mercury in fish tissues can also be put into perspective and evaluated with regard to a mercury risk to wildlife. The U.S. Fish and Wildlife Service (USFWS) has proposed a predator protection criterion of 100 ng/g THg in prey species (Eisler, 1987). More recently, in its Mercury Study Report to the U.S. Congress, USEPA proposed 77 ng/g and 346 ng/g for trophic level (TL) 3 and 4 fish, respectively, for the protection of piscivorous avian and mammalian wildlife (USEPA, 1997). STA-6 mosquitofish collected during the reporting year, which are considered to be at TL 2 to 3, depending on age (Loftus et al., 1998), contained Hg at concentrations much less than the USFWS and USEPA criteria. Sunfish from STA-6, which are at TL 3 (*L. gulosus* at TL 4; Loftus et al., 1998), contained levels of Hg that approached or exceeded the USEPA criteria but, on average, were less than the USFWS criteria. After adjusting arithmetic mean Hg concentrations in fillets to whole-body concentrations (whole-body THg concentration =  $0.69 \times$  fillet THg; Lange et al., 1998), largemouth bass in the discharge canal of STA-6 continued to exceed the USEPA's guidance value for TL 4 fish. Based on these criteria, fish-eating wildlife, if feeding preferentially at STA-6, appear to be at some risk of adverse chronic effects from mercury exposure. However, to date the District has not performed a formal assessment of the site-specific risks of MeHg toxic effects to fish-eating birds and mammals foraging preferentially in STA-6, and none is now planned.

THg concentrations in fish collected from STA-6 were substantially greater (up to five times greater) than levels observed at STA-1W, which subsumed the prototype STA (the ENR Project) (Table 5). However, concentrations of Hg in STA-6 fishes were comparable to levels observed in other areas of the Everglades (see Appendix 2B-3) and, thus, may reflect the overall mercury conditions in South Florida rather than being a consequence of STA operation.

## STA-5

As stated above, STA-5 met startup criteria for mercury in September 1999, and routine monitoring began during the first quarter of 2000. However, because of drought conditions and the detection of high phosphorus concentrations at the outflows, STA-5 did not begin flow-through operation until July 7, 2000. Results of monitoring prior to April 30, 2001 have been reported previously (Rumbold and Rawlik, 2000; Rumbold et al., 2001a; Rumbold and Fink, 2002; Rumbold and Fink, 2003).

As shown in Table 1 and Figure 7, THg in STA-5 outflow increased dramatically in the second quarter and then again in the third quarter of 2002. Obviously, this is similar to what occurred at STA-6, which is located just a few miles south of STA-5. Like STA-6, the spikes in THg followed rainfall events (5 in of rain fell in the month prior to both second and third quarter samples). But that is where the similarities end. Unlike STA-6, STA-5 showed no corresponding



**Figure 7.** Concentration of (a) total mercury (THg) and (b) methylmercury (MeHg) in unfiltered surface water collected at STA-5.

spike in MeHg. This crucial difference may, in part, be due to the fact that STA-5 had not suffered an extended drydown as did STA-6. Cell 2B did have a drawdown to near grade for ten days in the month prior to the second quarter collection. However, the other three cells had an average depth of approximately 1 ft during the month prior to the collection. One could speculate that because there was no drydown and oxidation of organic sulfur compounds, there was no sulfate stimulation of the sulfate-reducing bacteria (SRB). Another interesting point is that the variability shown in **Figure 7** (standard deviations in panel a), was not between cells as might have been expected but rather between culverts within cells. In the second quarter samples, THg concentrations were 5.9 ng/L and 0.78 ng/L at the two outflow culverts of Cell 1B (i.e., culverts G-344A and G-344B, respectively), and 7.4 ng/L and 1 ng/L at the two outflow culverts of Cell 2B (i.e., G-344C and G-344D, respectively; for map, see **Figure 2**). Between-culvert variability also occurred in the third quarter, but the pattern differed slightly. THg concentrations were 3.6 ng/L and 9.2 ng/L in the outflow of Cell 1B (i.e., concentration was substantially greater at G-344B culvert), and 7.1 ng/L and 3.1 ng/L in the outflow of Cell 2B. This difference between STA-5 culverts is even more interesting given the similarity in THg concentrations recorded at the outflow culverts of STA-6 Cell 5 (see discussion above). MeHg concentrations showed very little variability among STA-5 outflow culverts, however.

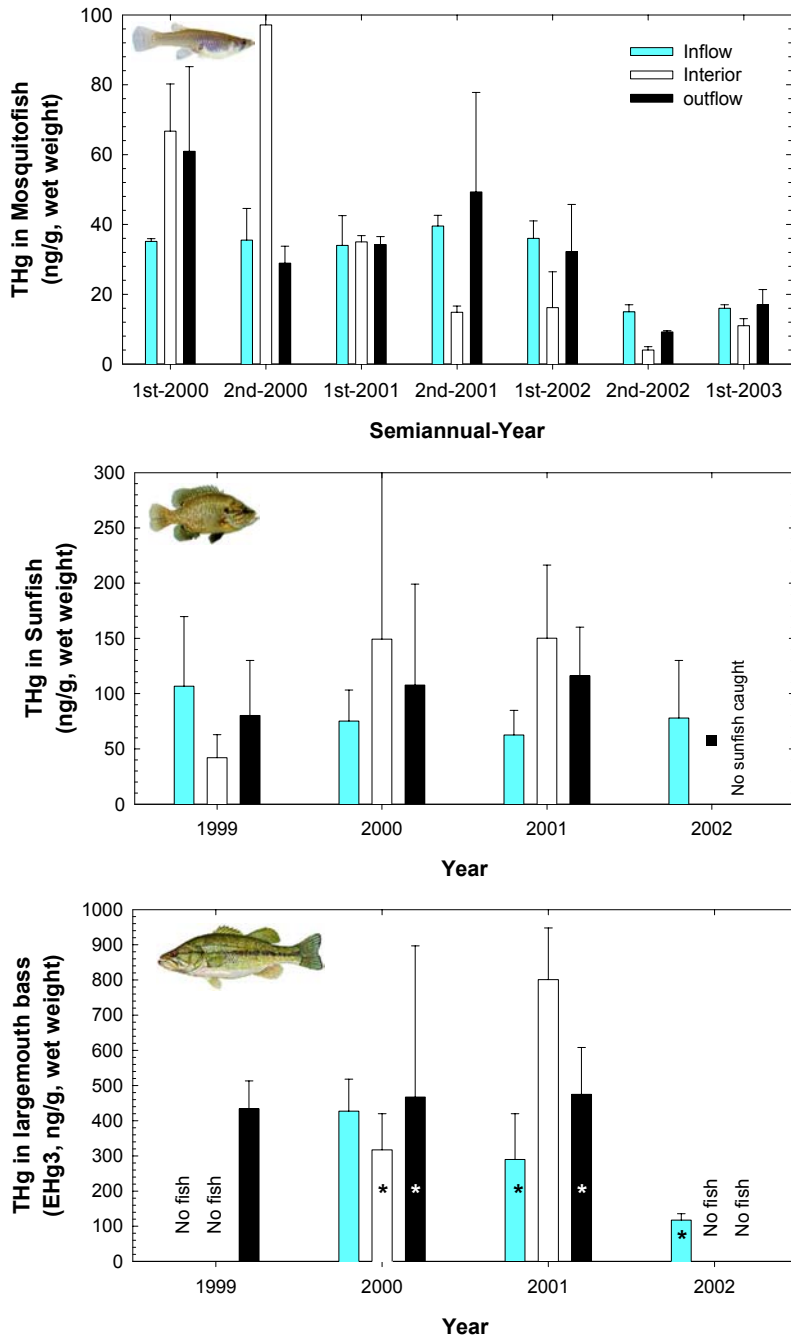
As a consequence of the spikes in the outflow during the second and third quarters, STA-5 exhibited a positive percent change in THg across the STA (**Table 1**). However, at no time during the reporting year did THg concentration exceed the Class III water quality standard of 12 ng/L. Although MeHg concentrations did not spike, a slightly positive percent change in MeHg occurred across the STA.

Results from operational monitoring of mercury concentrations in STA-5 mosquitofish are summarized in **Table 3** and **Figure 8**. Similar to what was observed in STA-6, levels of Hg in STA-5 mosquitofish were much lower than previous years. However, STA-5 mosquitofish continued to show the same spatial pattern as observed in previous years, i.e., fish from the interior marshes contained about 50 percent less Hg than fish from either the inflows or outflows. Hg levels in mosquitofish composites from the two internal marsh sites were similar (**Figure 8**).

Regrettably, few large-bodied fish were caught in STA-5 this year as part of the annual mercury monitoring collection. The FWC, which is under contract to the District to electroshock and collect large-bodied fishes for Hg monitoring, reported the following:

Unlike previous years when fish samples were collected easily, this year we did not observe any largemouth bass and only 1 sunfish in both cells. In Cell 1B (site STA5C1B1), electrofishing all available water resulted in collection of one small warmouth....Finding alternative access to the rim canal was unsuccessful and electrofishing in other areas of Cell 2B proved unsuccessful. Largemouth bass and sunfish have, in previous years, been found in good numbers in the interior cells of STA-5; however, this year Florida gar [*Lepisosteus platyrhincus*], an indicator of low-oxygen conditions, was the predominant species encountered. Other important species encountered were the exotic Mayan cichlid [*Cichlasoma urophthalmus*] and suckermouth catfish (*Liposarcus* spp.).





**Figure 8.** Mercury concentrations in (*top*) mosquitofish composites (+ range), (*middle*) whole sunfish ( $\pm$  SD), and (*bottom*) fillets of largemouth bass ( $\pm$  95% CI or, if arithmetic, SD) collected at STA-5. Note: The latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (\*for details see **Table 4**), in which case the arithmetic mean is reported.

Consequently, little can be inferred regarding levels of mercury in sunfish or bass in 2002. Sunfish were present and caught from the supply canal, however (**Table 4** and **Figure 8**). Over the last four years, this sunfish population exhibited interannual differences in Hg levels (Kruskal-Wallis ANOVA on Ranks,  $H = 9.9$ ,  $df = 3$ ,  $p < 0.02$ ), with concentrations in 2001 lower than 1999 (Dunn's method,  $p < 0.05$ ); other pairwise comparisons were not significant. It is important to note also that a disproportionate number of red ear sunfish (*L. microlophus*) were collected in 2001 and, because this lepidomid species tends to bioaccumulate less Hg (most likely due to trophic differences), this may account for the observed lower mean concentration.

Only 13 largemouth bass were collected from STA-5's supply canal in 2002 (**Table 5** and **Figure 8**). The average age of these bass was a little over one year. Not surprisingly, the regression of tissue Hg on age was not statistically significant ( $df = 1, 12$ ;  $F = 3.64$ ,  $P = 0.83$ ), and consequently, an EHg3 could not be estimated. The average age of bass caught from the supply canal in 2001 was 1.8 years. Thus, the apparent reduction in Hg from 2001 to 2002 may have been a function of sampling different age cohorts. Clearly, without Hg data for large-bodied fishes from the internal marshes, it is impossible to evaluate risk to fish-eating wildlife, except to say that levels of tissue Hg in mosquitofish were well below the USEPA or USFWS guidance level.

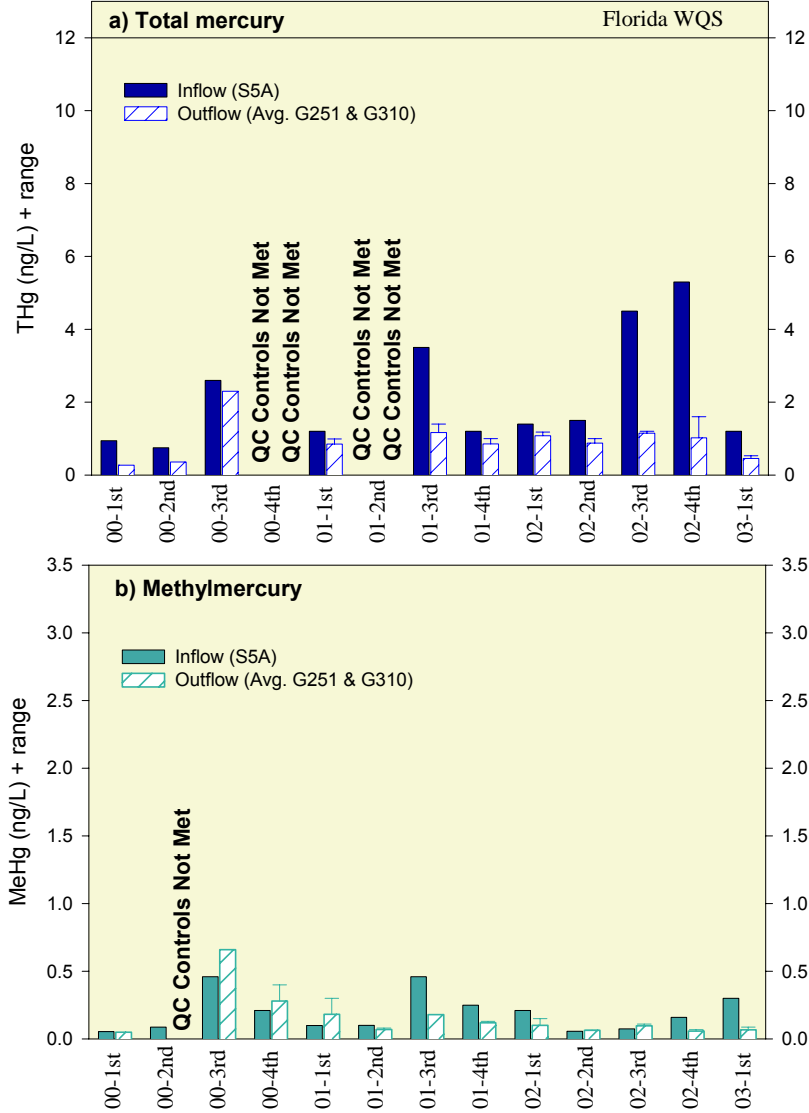
### STA-1W

Routine monitoring of mercury levels in surface waters of STA-1W began on February 16, 2000. Results of STA-1W monitoring prior to April 30, 2001 have been reported previously (Rumbold and Rawlik, 2000; Rumbold et al., 2001a; Rumbold and Fink, 2002; Rumbold and Fink, 2003).

As shown in **Table 1** and **Figure 9**, concentrations of both THg and MeHg in surface water at the outflows of STA-1W remained relatively low compared to the other STAs and compared to the inflow. Unlike STA-6 and STA-5, which exhibited spikes in outflow THg concentrations with the onset of the rainy season, STA-1W outflows remained relatively constant despite heavy rainfall events preceding sampling (3 in of rain within the 30 days preceding second- and fourth-quarter sampling) and despite increases in inflow THg. One plausible explanation might be that standing water in STA-1W diluted high concentrations of inorganic mercury in rainfall. The average depth of standing water in the STA during the 30 days prior to sampling was over 1 ft in the second quarter and between 2 ft and 3 ft during the third and fourth quarters. Although this theory seems reasonable for the second and third quarters, especially in comparison to the drydown and subsequent reflooding of STA-6, it is inconsistent with what was observed at STA-5. Recall that STA-5 exhibited spikes in THg, even though three of the four cells had approximately 1 ft of water. Therefore, beyond a dilution effect, it may be that STA-1W differs from the other STAs in the way new Hg (in rainfall) is assimilated. A similar finding may account for the between-cell differences in THg in STA-2 (see Appendix 4A-7).

Both THg and MeHg were generally at lower concentrations in surface water at the outflows than at the inflow. The exception was MeHg in the second and third quarters, when concentrations were slightly higher at the outflow as compared to the inflow. Nevertheless, on an annual basis, MeHg exhibited a strong negative percent change across the STA (**Table 1**). This is consistent with the removal efficiency that was routinely observed for the ENR Project, which was subsumed by STA-1W (SFWMD, 1999b).

### STA 1W Surface Water



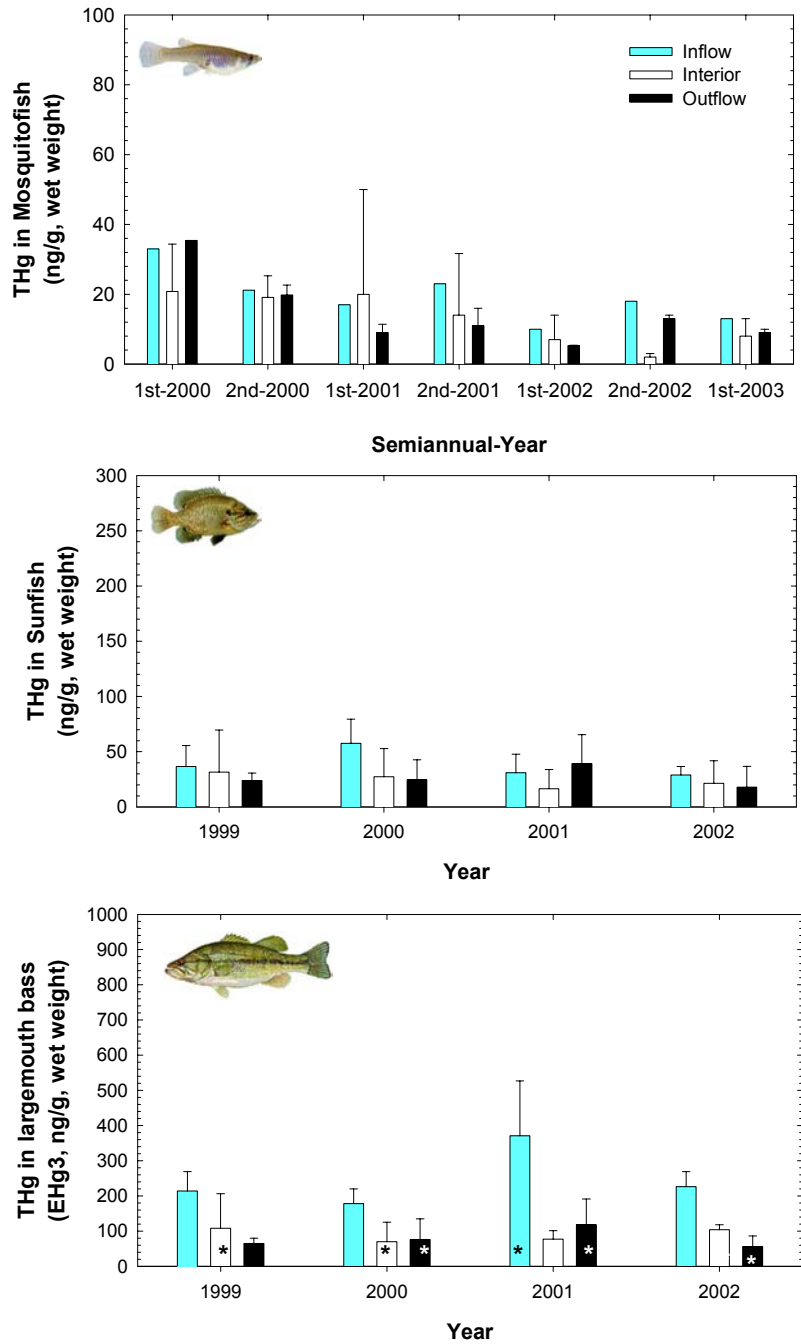
**Figure 9.** Concentration of (a) total mercury (THg) and (b) methylmercury (MeHg) in unfiltered surface water collected at STA-1W.

Concentrations of THg in mosquitofish are summarized in **Table 3** and are graphically presented in **Figure 10**. Levels of mercury in mosquitofish from STA-1W were similar to, or have declined slightly, when compared to concentrations observed in fish collected previously from this area when it was operated as the ENR Project (SFWMD, 1999b). Furthermore, Hg levels in STA-1W mosquitofish continue to be relatively low compared to other areas of the Everglades (see Appendix 2B-3). Similar to water column concentrations, mosquitofish also consistently exhibited a negative percent change in tissue Hg across STA-1W, with fish collected at the outflow containing about 30 percent less mercury than that of fish collected at the inflow (**Table 3**). As discussed below, this pattern, which was unparalleled in the other STAs, was also observed in sunfish and largemouth bass.

As is evident from **Table 4** and **Figure 10**, STA-1W sunfish continued to have mercury levels much lower than those observed in sunfish at the other STAs and at locations within the Everglades (Appendix 2B-3). This pattern does not appear to be changing, i.e., there have been no obvious increases over time (**Figure 10**). By comparison, STA-1W sunfish did exhibit a significant spatial pattern (i.e., locational differences) in tissue Hg in 2002 ( $H = 52.26$ ,  $df = 5$ ,  $P < 0.001$ ). Post hoc pairwise comparisons (Dunn's Method) revealed that fishes from Cell 5 contained Hg levels similar to that of fishes from the supply canal (i.e., upstream of S-5A). However, these two populations contained higher Hg levels than fishes from other interior marshes and as compared to fishes in the two discharge canals ( $P < 0.05$ ). This spatial pattern was not explained by distribution of species of lepomids collected nor by among-cell differences in sunfish size, as size did not differ significantly ( $F = 1.67$ ,  $df = 5$ ,  $111$ ;  $P = 0.147$ ). The spatial pattern in Hg was consistent with previous observations (Rumbold and Fink, 2003). Furthermore, when data from the last four years were pooled, Hg levels in Cell 5 sunfish were greater than levels in fishes from the other marshes ( $H = 105.7$ ,  $df = 2$ ,  $P < 0.001$ ).

Similar to sunfish, largemouth bass from STA-1W contained lower levels of Hg than bass from the other STAs (**Table 5** and **Figure 10**). Moreover, Hg in bass from STA-1W was also much lower than levels observed in fish from downstream sites in the WCAs (see Appendix 2B-3). As with mosquitofish and sunfish, Hg in bass exhibited a negative percent change across STA-1W, that is, it declined from the supply canal to discharge canals (-77 percent based on nonstandardized concentrations). The regression of Hg concentration on age was not significant for the outflow populations, either at individual sites (ENR012:  $df = 1$ ,  $10$ ;  $F = 0.17$ ,  $P = 0.68$ ; G-310:  $df = 1$ ,  $18$ ;  $F = 2.56$ ,  $P = 0.13$ ), or when populations from the two discharge canals were pooled ( $df = 1$ ,  $30$ ;  $F = 0.86$ ,  $P = 0.36$ ). Thus, an EHg3 could not be estimated. However, the regression was significant for the bass population sampled at the inflow, and this can be used to estimate a tissue concentration for comparison with outflows. The arithmetic mean of 56 ng Hg/g in bass from the outflows, which on average were two years old (**Table 5**), was substantially less than the 103 ng Hg/g that was estimated for a two-year-old bass at the inflow (i.e., based on the regression).

In terms of the risk to fish-eating wildlife, STA-1W mosquitofish, sunfish, and largemouth bass continue to have tissue-Hg levels well below both the USEPA and USFWS guidance level for predator protection. Therefore, unlike in most Everglades areas, fish-eating wildlife foraging preferentially at STA-1W do not appear to be at risk from Hg exposure.



**Figure 10.** Mercury concentrations in (top) mosquitofish composites (+ range), (middle) whole sunfish ( $\pm$  SD), and (bottom) fillets of largemouth bass ( $\pm$  95% CI or, if arithmetic, SD) collected at STA-1W. Note: the latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (\*for details, see **Table 5**), in which case, the arithmetic mean is reported.

## STA-2

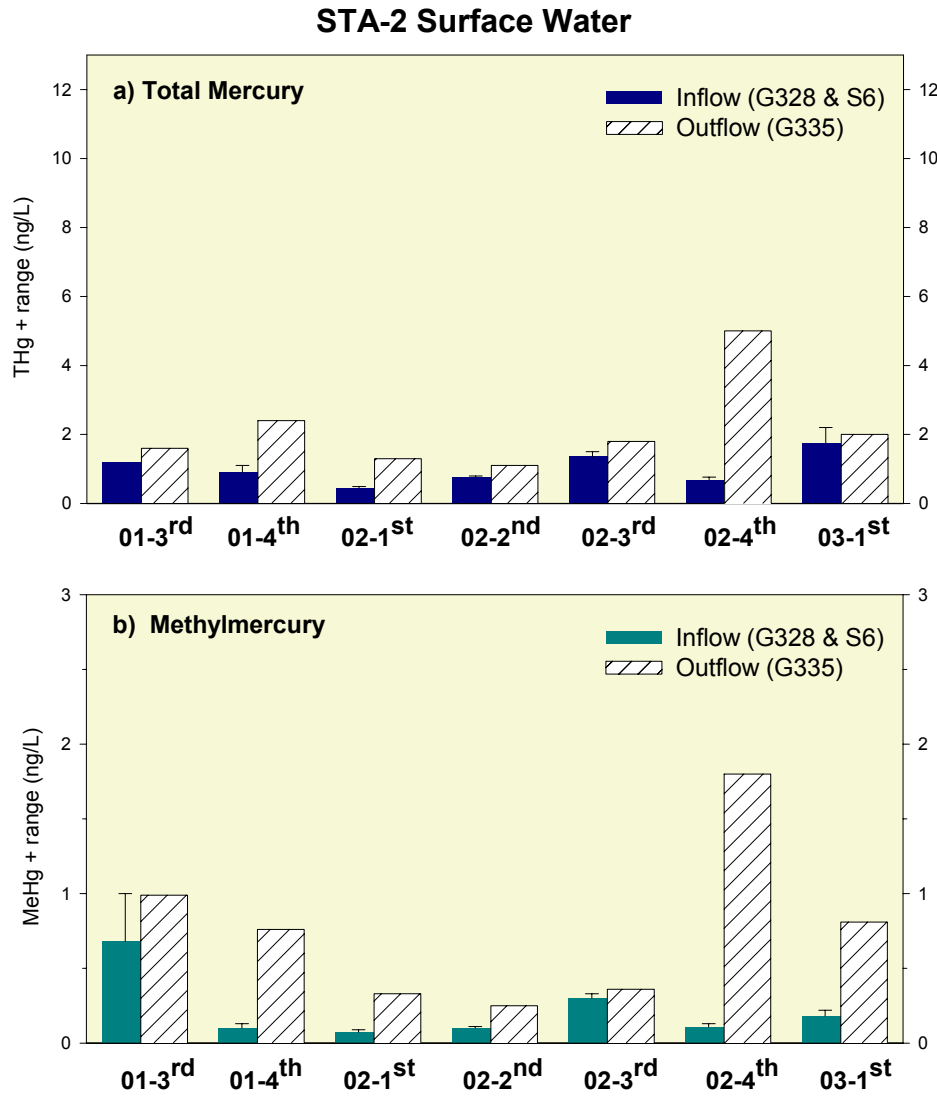
Operational monitoring of mercury at STA-2 began during the third quarter of 2001 following the completion of the S6 connection in May 2001 (for previously reported results, see Rumbold and Fink, 2003).

As is evident from data shown in **Table 1** and **Table 2**, which are graphically presented in **Figure 11**, water column concentrations of THg and MeHg were consistently greater at the outflow (G-335) than the inflow (S6 and G-328). (For mass budget, loading estimates, and discussion of influential factors, see Appendix 4A-7.) This positive percent change in THg and MeHg across the STA was most pronounced in the fourth quarter, when concentrations in the outflow peaked at 5 ng THg/L and 1.8 ng MeHg/L. At that time, MeHg was more than 16 times more concentrated in the outflow than in the inflow (a 1,567 percent change, **Table 2**). However, at no time during the reporting year did THg concentration exceed the Class III water quality standard of 12 ng/L.

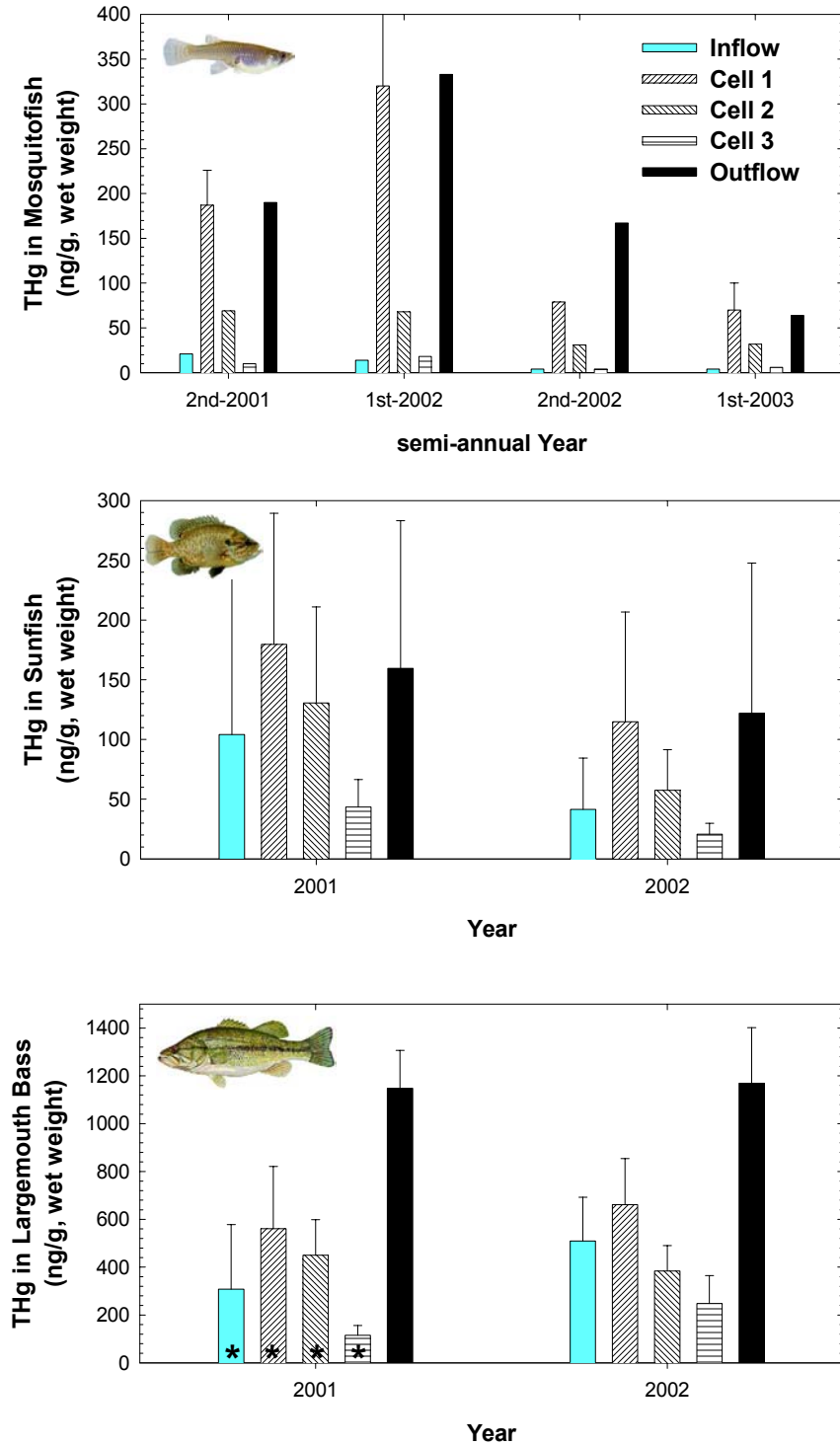
Results from operational monitoring of mercury concentrations in STA-2 mosquitofish are summarized in **Table 3** and **Figure 12**. (Note that the results from different interior sites are graphed separately because of the degree of spatial variability known to occur in this STA.) As evident from **Figure 12**, spatial patterns have been consistent over time with tissue Hg at very low levels in mosquitofish collected from the supply canal (at G-328B) and Cell 3, slightly higher in fish from Cell 2, and highest in fish residing in the discharge canal and Cell 1. This was a positive percent change across the STA. As discussed previously (Rumbold and Fink, 2003), due to the configuration of the G-330 outflow culverts, fish populations within Cell 1 may be able to mix with populations in the discharge canal. Most importantly, it should be noted that tissue Hg levels have declined in mosquitofish substantially over previous years (**Figure 12**) (also see Rumbold and Fink, 2003). Nevertheless, levels of mercury in mosquitofish from certain sites within STA-2 were elevated compared to the other STAs and to several downstream sites (**Table 3**). For comparisons to downstream sites, see Appendix 2B-3.

Spatial patterns in tissue Hg in sunfish were identical to those observed for mosquitofish (**Figure 12**); tissue-Hg levels were very low in sunfish collected from the supply canal and Cell 3, slightly higher in fish from Cell 2, and highest in fishes inhabiting the discharge canal and Cell 1. When results were pooled over the two-year period, these location-related differences were statistically significant (ANOVA on Ranks,  $H = 68.8$ ,  $df = 4$ ,  $P < 0.001$ ). Mercury levels in Cell 3 fish did not differ from fish in the supply canal; Hg levels in Cell 2 fish were greater than fish from either Cell 3 or the supply canal, but they did not differ from fish from Cell 1 or from the discharge canal. Fish from Cell 1 and the discharge canal did not differ from each other, but they contained significantly greater concentrations than fish inhabiting Cell 3 and the supply canal (based on Dunn's pairwise comparisons with  $\alpha = 0.05$ ). There were no similar location-related differences in fish size (weight: ANOVA on Ranks,  $H = 6.1$ ,  $df = 4$ ,  $P = 0.192$ ) or obvious differences in lepomid species caught that might explain the spatial patterns in tissue Hg.

In terms of temporal trends, interestingly, sunfish size (i.e., weight) increased in 2002 over 2001 at all sites. This suggests that these fish were older and had a longer period of exposure (sunfish were not aged). Yet, at the same time, Hg body burden generally decreased in 2002 (**Figure 12**). This between-year difference in Hg level was significant for fish in the supply canal (Mann-Whitney Rank sum test,  $p = 0.3$ ), Cell 3 ( $p = 0.001$ ), Cell 2 ( $p < 0.001$ ), and Cell 1 ( $p = 0.03$ ) but not in the discharge canal ( $p = 0.12$ ). However, caution must be exercised when interpreting Cell 1 results. In 2001, both sunfish and bass were collected from the southern end of Cell 1 (designated site C1X). In 2002, despite a good-faith effort, the FWC was unable to collect



**Figure 11.** Concentration of (a) total mercury (THg) and (b) methylmercury (MeHg) in unfiltered surface water collected at STA-2.



**Figure 12.** Mercury concentrations in (*top*) mosquitofish composites (+ range), (*middle*) whole sunfish ( $\pm$  SD), and (*bottom*) fillets of largemouth bass ( $\pm$  95% CI or, if arithmetic, SD) collected at STA-2. Note: the latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (\*for details, see **Table 5**), in which case the arithmetic mean is reported.



sufficient numbers of fish in the southern end (only three fish were caught during 30 minutes of pedal time and were subsequently released). Therefore, FWC shocked and caught both sunfish and bass from the northern end of the cell (T. Lange, FWC report dated January 3, 2003). Given the known positive gradient in Hg from north to south in Cell 1 and the proximity of the 2002 collection site to the inflow culverts (which raises the possibility of catching fish from the supply canal recently invading the cell), the representativeness of the 2002 samples from Cell 1 are uncertain.

Unlike mosquitofish, levels of mercury in sunfish from STA-2 were only slightly elevated when compared to fish at other STAs (**Table 4**). Furthermore, STA-2 sunfish contained less mercury than fish from many downstream sites (for comparisons to downstream sites, see Appendix 2B-3). This is an important observation given the relative levels observed in the mosquitofish and, as discussed below, the bass. At this point in time, any attempt to account for this inconsistency would be speculative.

Results from operational monitoring of mercury concentrations in largemouth bass from STA-2 are summarized in **Table 5** and are graphically displayed in **Figure 12**. Spatial patterns in mercury levels in largemouth bass were very similar to those observed in sunfish and mosquitofish. The only possible exception was that levels of mercury in bass in the discharge canal and in Cell 1 were more dissimilar than other species. Similar to sunfish, the positive percent change in tissue Hg in the bass across the STA was dramatic, going from 509 ng/g in supply canal fish to 1,169 ng/g in discharge canal fish (a 316 percent increase, **Table 5**).

However, some caution must be exercised when interpreting the bass results. First, in 2001, data were sufficient to calculate an EHg3 only for bass in the discharge canal. Ages of the bass captured from other sites were too narrow to establish a good regression (median ages were 1.8 years). Second, in 2002, although age distributions were satisfactory and EHg3 values were reported for all sites, several data sets were not normally distributed (for tissue Hg in fish from the supply canal, Cell 3, and Cell 2) and, thus, EHg3 values are considered tentative. Hence, use of ANCOVAs was also inappropriate. Finally, as discussed earlier with regard to sunfish, bass were not captured at the same sites in Cell 1 in 2001 and 2002, and because of previously discussed uncertainties, temporally trend analysis was therefore not appropriate. Examining between-year differences in Hg levels in bass from the discharge canal was valid and was found not to be significant (ANCOVA, df 1, 37;  $F = 0.01$ ;  $p = 0.94$ ).

Clearly, levels of mercury were elevated in STA-2 bass, especially bass from the discharge canal, as compared to other STAs (**Table 5**) and downstream sites (see Appendix 2B-3). Only two downstream sites, CA3-15 and L67F1, both known MeHg “hotspots,” had fish with levels of mercury similar to the fish in the discharge canal of STA-2. Most importantly, the EHg3 in largemouth bass collected from the discharge canal exceeded Florida’s fish consumption advisory threshold of 0.5 ppm by more than a factor of two.

In terms of the risk to fish-eating wildlife, mosquitofish from Cell 1 and the discharge canal contained Hg at concentrations above both the USFWS (100 ng/g) and USEPA criteria (77 ng/g). Likewise, after adjusting arithmetic mean Hg concentrations in fillets to whole-body concentrations (whole-body THg concentration =  $0.69 \times$  fillet THg; Lange et al., 1998), largemouth bass from Cell 1 and the discharge canal also exceeded USEPA’s guidance value for TL 4 fish. In contrast, levels of mercury in STA-2 sunfish, even those caught in Cell 1 and the discharge canal, were below the USEPA criteria for TL 3 fish. Because sunfishes are a preferred prey item for a number of wildlife species and, thus far, have not biomagnified mercury to the same degree that the mosquitofish and bass have, risk to wildlife is not as great as it might have

been. Nevertheless, fish-eating wildlife still appear to be at some risk of adverse chronic effects from mercury exposure, especially if feeding preferentially on mosquitofish or small bass.

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